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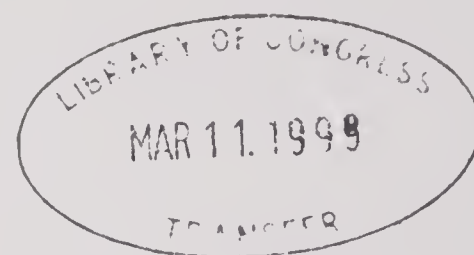
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Oxygenates in Water: Critical Information and Research Needs



Oxygenates in Water: Critical Information and Research Needs

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460



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U.S. Environmental Protection Agency Task Group

Principal Authors

J. Michael Davis (Chair)
Office of Research and Development
National Center for Environmental
Assessment
Research Triangle Park, NC 27711

John Brophy
Office of Air and Radiation
Office of Mobile Sources
Washington, DC 20001

Robert Hitzig
Office of Solid Waste and Emergency
Response
Office of Underground Storage Tanks
Washington, DC 20460

Fran Kremer
Office of Research and Development
National Risk Management Research
Laboratory
Cincinnati, OH 45268

Michael Osinski
Office of Water
Office of Groundwater and Drinking Water
Washington, DC 20460

James D. Prah
Office of Research and Development
National Health and Environmental
Effects Research Laboratory
Research Triangle Park, NC 27711

Stephen Schmelling
Office of Research and Development
National Risk Management Research
Laboratory
Ada, OK 74821-1198

Thomas F. Speth
Office of Research and Development
National Risk Management Research
Laboratory
Cincinnati, OH 45268

Robert Swank
Office of Research and Development
National Exposure Research Laboratory
Athens, GA 30605-2720

Anthony N. Tafuri
Office of Research and Development
National Risk Management Research
Laboratory
Edison, NJ 08837

Candida West
Office of Research and Development
National Risk Management Research
Laboratory
Ada, OK 74821-1198

Contributors

Dorothy Canter
Office of Solid Waste and Emergency
Response
Office of the Assistant Administrator
Washington, DC 20460

Stanley Durkee
Office of Research and Development
Office of Science Policy
Washington, DC 20460

U.S. Environmental Protection Agency Task Group
(cont'd)

Contributors (cont'd)

Jackson Ellington
Office of Research and Development
National Exposure Research Laboratory
Athens, GA 30605-2720

Charles Freed
Office of Air and Radiation
Office of Mobile Sources
Washington, DC 20001

Frank Gostomski
Office of Water
Office of Science and Technology
Washington, DC 20460

Judith A. Graham
Office of Research and Development
National Exposure Research Laboratory
Research Triangle Park, NC 27711

Matthew Hagemann
Region 9
San Francisco, CA 94105

John Helvig
Region 7
Kansas City, KS 66101

Roland Hemmet
Region 2
New York, NY 10007-1866

Robert W. Hillger
Region 1
Boston, MA 02203

Kenneth T. Knapp
Office of Research and Development
National Exposure Research Laboratory
Research Triangle Park, NC 27711

Amal Mahfouz
Office of Water
Office of Science and Technology
Washington, DC 20460

Michael Moltzen
Region 2
New York, NY 10007-1866

Richard Muza
Region 8
Denver, CO 80202

Charles Ris
Office of Research and Development
National Center for Environmental
Assessment
Washington, DC 20460

Bill Robberson
Region 9
San Francisco, CA 94105

Gary Timm
Office of Prevention, Pesticides, and
Toxic Substances
Washington, DC 20460

Jim Weaver
Office of Research and Development
National Exposure Research Laboratory
Athens, GA 30605-2720

Lester Wyborny II
Office of Air and Radiation
Office of Mobile Sources
Ann Arbor, MI 48105-2498

U.S. Environmental Protection Agency Task Group
(cont'd)

Members

Charles Auer
Office of Prevention, Pesticides, and
Toxic Substances
Washington, DC 20460

Ben Blaney
Office of Research and Development
National Risk Management Research
Laboratory
Cincinnati, OH 45268

Dave Brown
Office of Research and Development
National Exposure Research Laboratory
Athens, GA 30605-2720

Rebecca L. Calderon
Office of Research and Development
National Health and Environmental Effects
Research Laboratory
Research Triangle Park, NC 27711

Tudor Davies
Office of Water
Office of Science and Technology
Washington, DC 20460

Joe A. Elder
Office of Research and Development
National Health and Environmental Effects
Research Laboratory
Research Triangle Park, NC 27711

William H. Farland
Office of Research and Development
National Center for Environmental
Assessment
Washington, DC 20460

Rene Fuentes
Region 10
Seattle, WA 98101

Lester D. Grant
Office of Research and Development
National Center for Environmental
Assessment
Research Triangle Park, NC 27711

Fred Hauchman
Office of Research and Development
National Health and Environmental Effects
Research Laboratory
Research Triangle Park, NC 27711

Steven F. Hedtke
Office of Research and Development
National Health and Environmental Effects
Research Laboratory
Duluth, MN

John Heffelfinger
Office of Solid Waste and Emergency
Response
Office of Underground Storage Tanks
Washington, DC 20460

Ronald Landy
Region 3
Philadelphia, PA 19107

Maureen Lewison
Office of Solid Waste and Emergency
Response
Office of Underground Storage Tanks
Washington, DC 20460

U.S. Environmental Protection Agency Task Group
(cont'd)

Members (cont'd)

Dennis McChesney
Region 2
New York, NY 10007-1866

Winona Victory
Region 9
San Francisco, CA 94105

John Mooney
Region 5
Chicago, IL 60604-3507

Michael Watson
Region 10
Seattle, WA 98101

Margo Oge
Office of Air and Radiation
Office of Mobile Sources
Washington, DC 20460

Jeanette Wiltse
Office of Water
Office of Science and Technology
Washington, DC 20460

Charles Sands
Office of Solid Waste and Emergency
Response
Washington, DC 20460

Lynn Wood
Office of Research and Development
National Risk Management Research
Laboratory
Ada, OK 74821-1198

Paul Scoggins
Region 6
Dallas, TX 75202-2733

Donn Zuroski
Region 9
San Francisco, CA 94105

External Reviewers*

David Ashley
National Center for Environmental Health
U.S. Centers for Disease Control and
Prevention
Atlanta, GA 30341-3724

Bruce Bauman
American Petroleum Institute
Washington, DC 20005-4070

Steven Book
California Department of Health Services,
Drinking Water
Sacramento, CA 94234-7320

Robert Borden
North Carolina State University
Raleigh, NC 27695

Susan Borghoff
Chemical Industry Institute of Toxicology
Research Triangle Park, NC 27709-2137

Herb Buxton
Toxic Substances Hydrology Program
U.S. Geological Survey
West Trenton, NJ 08628

Maria Costantini
Health Effects Institute
Cambridge, MA 02139-3180

James S. Crowley
Santa Clara Valley Water District
San Jose, CA 95118-3686

Joan Denton
California Air Resources Board
Sacramento, CA 95814

Gary Ginsberg
Connecticut Department of Public Health
Hartford, CT 06134-0308

Bernard Goldstein (Workshop Chair)
Department of Environmental Community
Medicine
Environmental and Occupational Health
Sciences Institute
Piscataway, NJ 0885-1179

Anne Happel
Environmental Restoration Division
Lawrence Livermore National Laboratory
Livermore, CA 94551

Carol Henry
American Petroleum Institute
Washington, DC 20005-4070

Michael Kavanaugh
Malcolm Pirnie, Inc
Oakland, CA 94612

John Kneiss
Oxygenated Fuels Association
Arlington, VA 22209

Jerold Last
UC Toxic Substances Research and
Teaching Program
University of California-Davis
Davis, CA 95616-8723

Ronald Melnick
National Institute of Environmental Health
Sciences
Research Triangle Park, NC 27709

James Pankow
Oregon Graduate Institute
Portland, OR 97291-1000

Hari Rao
Edison, NJ 08820

External Reviewers
(cont'd)

Thomas Skower
Underwriters Laboratories, Inc.
Northbrook, IL 60062

Arthur Stewart
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6036

John H. Sullivan
Government Affairs Office
American Water Works Association
Washington, DC 20005

Robert Tardiff
Sapphire Group, Inc.
Bethesda, MD 20814

Barbara Walton / Rosina M. Bierbaum
Office of Science and Technology
Policy - Environment Division
Executive Office of the President
Washington, DC 20502

Clifford Weisel
Exposure Measurement and Assessment
Division
Environmental and Occupational Health
Sciences Institute
Piscataway, NJ 08855-1179

John Zogorski
U.S. Geological Survey
Water Resources Division
Rapid City, SD 57702

*These individuals provided technical review comments by invited participation in a review workshop held on October 7, 1997 and/or by written submissions.

Preface

The purpose of this document is to identify key issues related to assessing and managing the potential health and environmental risks of oxygenate contamination of water. Oxygenates are chemicals added to fuels (“oxyfuels”) to increase the oxygen content and thereby reduce emissions from use of the fuel. This document builds on and extends an earlier report, *Oxyfuels Information Needs* (U.S. Environmental Protection Agency, 1996), which included water issues but tended to focus more on inhalation health risk issues. The present document focuses on those gaps and limitations in current information that constitute the most critical and immediate needs to be addressed in support of risk assessment and risk management efforts related to oxygenates in water. This document is primarily intended to serve as a starting point and general guide to planning future research. It is not a comprehensive review of issues pertaining to oxygenates in water, nor does it describe in detail specific studies or projects that are needed.

Efforts to address many of the needs identified in this document have already begun or are under consideration by various organizations. A current listing of such projects may be found in Appendix 2.

1. INTRODUCTION

Contamination of ground and surface waters by motor vehicle fuels and fuel additives is not a new problem, given the history and pervasive use of fuels in the 20th century. Well over a million underground fuel storage tanks exist in the United States, and leaks from these tanks have been the focus of major programs to prevent or clean up such releases. Transport of fuels via pipelines and in bulk containers also presents the potential for accidental releases and consequent environmental contamination. Experience suggests that contamination from these and other sources of fuel releases can affect water quality and the biota that depend upon the water, including human populations.

Against this background of experience with fuel-related contamination of ground and surface waters, recent events have focused attention on what appear to be somewhat different characteristics associated with fuels containing chemicals known as oxygenates. Oxygenates are added to fuel to increase its oxygen content and thereby reduce certain emissions from use of the fuel. Of the several ethers and alcohols that may serve as oxygenates, methyl tertiary butyl ether (MTBE) is the most frequently used. Monitoring of groundwater quality by the U.S. Geological Survey (USGS) indicates that MTBE has become detectable in shallow groundwater samples in certain urban areas in recent years, with concentrations ranging from below the reporting level of $0.2 \mu\text{g/L}$ ¹ to over $20,000 \mu\text{g/L}$ (Squillace et al., 1996). Reports of point-source MTBE contamination of drinking water sources at well over $100 \mu\text{g/L}$, including aquifers serving as the primary source of drinking water for the city of Santa Monica, CA (California Department of Health Services, 1998), raise several important questions about potential environmental and public health impacts of oxygenated fuels.

A key question is whether oxygenates in water pose a significant threat to human health or the environment. To assess the risks of MTBE or any other oxygenate, the potential for exposure to, and effects of, the contaminant(s) must be characterized. However, only limited information exists for characterizing the possible risks of oxygenates in water. For example, the extent of population exposures to MTBE in drinking water is unknown. Even in cases where MTBE is clearly present in public or private water supplies, limited guidance exists for determining levels

¹ $1 \mu\text{g/L} = 1$ part per billion (ppb).

that would be acceptable or unacceptable from the standpoint of public health or consumer acceptability. The U.S. Environmental Protection Agency (EPA) Office of Water has released a Drinking Water Advisory for MTBE (U.S. Environmental Protection Agency, 1997). As the full title of the document indicates, it provides “Consumer Acceptability Advice and Health Effects Analysis on [MTBE].” The Advisory “recommends that keeping levels of contamination in the range of 20 to 40 µg/L or below to protect consumer acceptance of the water resource also would provide a large margin of exposure (safety) from toxic effects.” However, the document discusses “many uncertainties and limitations associated with the toxicity data base for this chemical” and notes the consequent difficulty in estimating a health protection level for MTBE in drinking water. The uncertainties in assessing the health risks of MTBE are reflected somewhat in the various guidance values (e.g., advisories, action levels, standards) that have been issued by individual states, ranging at one time from 35 µg/L in California to 230 µg/L in Illinois (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). As efforts to assess health risks and derive guidance values continue at the local, state, and federal levels, the need for an adequate scientific foundation for these efforts intensifies. Without more definitive scientific information, uncertainties will continue to dominate risk assessments of oxygenates.

If it is concluded that a risk or problem exists, other questions face risk managers in formulating actions to address oxygenate contamination of water. For example, What are the sources of contamination? How long is it likely to persist? How widespread is the contamination? What cost-effective methods exist to remove the contaminant(s) from water? and, How can further contamination be avoided? A recent review of fuel oxygenates and water quality (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) notes that for various reasons, including the potentially greater persistence of MTBE in ground water than other components of gasoline, remediation of MTBE-contaminated ground water may pose unique problems. The Interagency Assessment also notes the possibility that ground water could be contaminated by deposition of oxygenates from the ambient atmosphere. A quantitative answer to whether non-point sources or point sources, such as leaking underground storage tanks (USTs), pose a greater potential risk of environmental contamination is not available.

Risk assessment and risk management require information that is generally obtained through research, data collection, or analysis of data that already exist. The purpose of this document is to identify the key information needed to assess and manage the potential health and environmental

risks related to oxygenates in water. This document builds on an earlier report, *Oxyfuels Information Needs* (U.S. Environmental Protection Agency, 1996), which encompassed water issues but tended to emphasize inhalation health risk issues. As noted in *Oxyfuels Information Needs*, the benefits and risks of any given oxyfuel must be assessed in relation to an alternative, such as conventional gasoline. A comparative assessment of the potential risks or benefits of any given fuel in relation to any other fuel is obviously a complex, multifaceted endeavor (see U.S. Environmental Protection Agency, 1992). The present document is much more limited in scope. It focuses on key information required to support the most pressing risk assessment and risk management needs pertaining to oxygenates in water, with the aim of achieving progress more readily than would be possible by attempting to cover every possible issue in a comprehensive manner. However, one should not lose sight of the broader and perhaps ultimate issue of the need to examine quantitatively the trade-offs between sought improvements in air quality through the use of oxygenates and possible reductions in water quality through oxygenate contamination.

This document is primarily intended to serve as a starting point and general guide to planning research related to oxygenates in water. It does not attempt to describe in detail specific studies and projects that are needed. Nor is this document a formal assessment of environmental or health risks associated with oxygenates or an in-depth analysis of candidate risk management options for addressing this problem. Other reports are available for more detailed reviews of the health and environmental effects of oxygenates (e.g., U.S. Environmental Protection Agency, 1993, 1994; Health Effects Institute, 1996; Interagency Oxygenated Fuels Assessment Steering Committee, 1996, 1997; National Research Council, 1996), particularly the "Water Quality" chapter from the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Note that all of these reports have pointed out the lack of adequate information to assess fully and definitively the risks and benefits associated with oxyfuels in comparison to conventional fuels.

Some brief background information on why fuel oxygenates are used may be helpful. The 1990 Clean Air Act Amendments (CAAA) created two fuel programs to be administered by EPA requiring use of oxygenates (U.S. Code, 1990). The first program began in the fall of 1992 with the objective of reducing carbon monoxide (CO) emissions in several areas of the country where the National Ambient Air Quality Standard (NAAQS) for CO was exceeded. Under this program, the CAAA required the sale of gasoline with an oxygen content of 2.7% by weight

during the cold weather season in designated areas that failed to attain the NAAQS for CO. The second program required the year-round use of reformulated gasoline (RFG) containing 2.0% oxygen by weight, beginning in 1995, in selected areas having the highest levels of tropospheric ozone. In addition to reducing emissions of ozone precursors, the RFG program also was intended to help reduce the emissions of certain toxic organic air pollutants. Collectively, cold-weather oxygenated gasoline and year-round RFG with oxygenate may be referred to as “oxyfuels.”

Although MTBE and, to a lesser extent, ethanol currently dominate the marketplace, no specific oxygenate is required or designated by the 1990 CAAA. Several other ethers and alcohols also may serve as oxygenates and could become more prevalent, depending on various factors such as cost, ease of production and transfer, and blending characteristics. These oxygenates include ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tertiary amyl ethyl ether (TAEE), diisopropyl ether (DIPE), dimethyl ether (DME), and tertiary butanol (TBA). The chemical properties of several oxygenates are listed in Appendix 1. To achieve the specified oxygen content requirements, approximately 15%-vol MTBE or 7.5%-vol ethanol can be used to yield the 2.7%-wt oxygen for the winter fuel program and approximately 11%-vol MTBE or 5.5%-vol ethanol for the 2.0%-wt oxygen required by the RFG fuel program.

According to EPA’s Office of Mobile Sources, about 30% of U.S. gasoline currently contains some form of oxygenate for air quality improvement purposes. Beginning in the late 1970s, MTBE and ethanol were used to increase the octane value of gasoline in the United States as lead was phased out. Approximately 25% or more of U.S. fuel may have contained MTBE or ethanol as an octane-enhancer in a given year, but the current usage of MTBE for octane is considerably lower, constituting perhaps 3 to 5% of the fuel supply. These levels of usage are subject to alteration as economic variables (e.g., the price of crude oil) and other factors change. The concentration of MTBE used for octane purposes in conventional gasoline may vary widely up to an allowable limit of 15%-vol MTBE, depending on other constituents and properties of the fuel, but likely is more on the order of 1 to 8%-vol MTBE. Gasoline containing 10% ethanol, often referred to as “gasohol,” represents about 10% of all gasoline sold in the United States, but may be much more prevalent in certain locales, particularly in the Midwest. More than 10 billion kg MTBE was used in U.S. gasoline in 1996, and fuel ethanol use was about 3 billion kg (DeWitt & Company, Incorporated, 1997).

This document applies to all ether and alcohol oxygenates unless otherwise stated. It refers more to MTBE because of its predominant use and because more information is available for MTBE than for other ethers and alcohols (except perhaps for ethanol). Nevertheless, it should not be inferred that the only oxygenate warranting attention is MTBE or, for that matter, that the issues identified here are necessarily unique to oxyfuels.

This document is organized around the following headings:

- Source Characterization
- Transport
- Transformation
- Occurrence
- Exposure
- Aquatic Toxicity
- Health Effects
- Release Prevention
- Contaminant Removal

Within each of these areas, a brief background section highlights available information on key issues, followed by a section that identifies research or other information gaps that emerge as needs. Note that the grouping of topics is somewhat arbitrary. The overlap in various areas should be seen as a potential benefit in terms of combining objectives and resources for projects that can be feasibly and appropriately linked. Such leveraging of resources could extend across organizational boundaries as well.

2. SOURCE CHARACTERIZATION

2.1 Background

Releases of fuel oxygenates occur during manufacture, distribution, storage, and use, particularly from point sources such as USTs, pipelines, and refueling facilities. According to the Toxics Release Inventory (TRI), releases of MTBE from production sources in the United States amounted to approximately 1.7 million kg in 1996 (U.S. Environmental Protection Agency, 1998a). Of this total, about 97% was released to the air and less than 3% was discharged to

surface water. For mobile sources, assuming 10 billion kg MTBE used in gasoline (DeWitt & Company, Incorporated, 1997) and an average U.S. corporate fleet emission rate of approximately 3.6 mg MTBE per gram MTBE in fuels (Wyborny, 1997, 1998), total motor vehicle emissions of MTBE in 1996 would have been on the order of 40 million kg in the United States.

Impacts to water resources can be loosely grouped into two categories: (1) widespread impacts occurring at low concentrations and (2) local impacts occurring at high concentrations. The first group is often the result of indirect sources, such as vehicular emissions of oxygenates that dissolve in rainfall and subsequently infiltrate to ground water, and may be spread over large areas. Also, leakage from motorized recreational water craft can be considered a diffuse source of contamination of surface water bodies such as reservoirs. The second category results from direct releases to surface and ground water from such sources as leaking USTs, pipelines, or tank cars.

Oxygenates in the atmosphere degrade with a half-life as short as 3 days (Smith et al., 1991; Wallington et al., 1988). However, MTBE is soluble in water and, because of its relatively low Henry's Law constant, partitions readily from air to rainfall and snowfall. The concentration in precipitation is determined primarily by the concentration in the atmosphere, the Henry's Law constant at a given air temperature, the time that the precipitation is exposed to MTBE, and other characteristics of the precipitation that determine contact efficiency, e.g., rain droplet size and snowflake surface area (Hoff et al., 1998). This process could result in deposition to land surface and subsequent contamination of surface and ground water. Also, MTBE could accumulate in snow at sites such as service stations, parking lots, and city streets and be released as a pulse source to soil or ground water as the snow melts. The detection of MTBE in 41 (7%) of 592 stormwater samples collected in 16 cities and metropolitan areas from 1991 to 1995, with the highest percentage of detections found in samples collected during high MTBE usage winter months (Delzer et al., 1996), is consistent with atmospheric washout of MTBE in rain or snow to the ground surface. Measured concentrations of MTBE in the stormwater samples ranged from 0.2 to 8.7 $\mu\text{g/L}$, with a median of 1.5 $\mu\text{g/L}$. Modeling calculations have predicted MTBE concentrations in rainwater ranging from <1 $\mu\text{g/L}$ to 3 $\mu\text{g/L}$, within the range of concentrations actually found in groundwater samples (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Also, modeling of the transport of MTBE from land surface to water table by

the infiltration of rain water, for a variety of infiltration and evapotranspiration scenarios, suggests that the concentration of MTBE in groundwater two meters below the water table can range from zero to almost 200 percent of the concentration in the rain water (Pankow et al., 1997). The use of shallow ground water for public and private water supplies makes such nonpoint contamination a potential public health issue as well as an environmental quality issue.

Direct releases of MTBE and other fuel oxygenates to surface and groundwater sources of drinking water also occur. The majority of direct releases of MTBE to surface water reported to TRI were attributable to only a few petroleum product facilities. However, refueling and operation of boats and other recreational water craft also are suspected as significant sources of releases of MTBE to surface waters in heavily used recreational areas. Detections of MTBE in some drinking water reservoirs in California have prompted studies on the input of MTBE to surface waters via recreational watercraft, precipitation, and snowmelt runoff (e.g., Reuter et al., 1998; Dale et al., 1997). Other possible sources of MTBE releases to surface water could include wastewater treatment operations at petroleum operations and publicly owned treatment works.

Leaking USTs are believed to be the primary source of localized releases of MTBE in high concentrations. According to EPA's Office of Underground Storage Tanks (OUST), nearly 1 million federally regulated USTs are currently in use at approximately 360,000 facilities in the United States. Not all of these USTs contain oxyfuels or gasoline with MTBE or ethanol as octane enhancers, but it can be roughly estimated that about 50% of the gasoline sold in the United States in recent years has contained MTBE or ethanol (U.S. Department of Energy, 1995). Some of the earliest documented UST releases involving MTBE occurred in Maine in the mid-1980s (Garrett, 1987). More recently, drinking water wells in Santa Monica, CA, were shut down because of MTBE contamination from one or more leaking USTs (Geraghty & Miller, Incorporated, 1996). Since 1988, 330,000 confirmed releases from regulated USTs have been reported to EPA/OUST. Based on historical trends, OUST estimates that 100,000 additional releases will be reported during the next few years as existing USTs are upgraded, closed, or replaced. This estimate does not include an even greater number of federally unregulated storage tanks. Although EPA regulations (§280.21, Code of Federal Regulations, 1990) require that all USTs be upgraded, closed, or replaced by December 1998, current estimates indicate that 25 to 35% of USTs will not be in compliance by that date.

Despite recent and ongoing studies, it is not clear whether the greater impact from MTBE or other fuel oxygenates to ground water is from diffuse or point sources (i.e., what fraction of the MTBE or other oxygenate load and exposure is diffuse [e.g., from precipitation] or is related specifically to spills or leaks from fuel containers). Although relatively high groundwater concentrations may be readily associated with point source releases, concentrations on the order of 10 µg/L or lower could be associated with nonpoint sources as well as point sources (Interagency Oxygenated Fuels Assessment Steering Committee, 1997).

2.2 Needs

A model linking air to land to surface water and ground water fate for oxygenates needs to be developed and tested. Such an airshed-watershed model could be used to conduct ecosystem exposure assessments, serve as a key input to human exposure assessments, design management and remediation strategies, and assist in source identification and apportionment. In particular, the model could be used to predict upper limit values of surface and ground water concentrations from ambient sources that could be compared to measured values, such as those expected from the ongoing USGS study at Glassboro, NJ (Baehr and Ayers, 1997). A recent review of the environmental behavior and fate of MTBE by Squillace et al. (1997) summarizes important transport and transformation processes that must be included in such a model. The model could build on recent work by Pankow et al. (1997) and Malcolm Pirnie, Incorporated (1998a) on modeling the ground water impacts from atmospheric washout and surface water impacts from the use of two-stroke engines. The model also could be used to estimate snow blanket buildup of oxygenates and subsequent release at first thaw, with the results then compared to data from field studies as a test of this potential pulse loading mechanism in a watershed. Once this modeling tool is developed and tested, it could be used to provide a national estimate of ambient contributions to surface and shallow ground water. It also could be used to provide point and non-point source aggregate concentrations within specific watersheds as a function of time (season) for total exposure assessment purposes.

The relative loads or fluxes of the oxygenates to surface and ground waters from point sources versus diffuse (nonpoint) sources must be more accurately determined. A possible approach to addressing this need might be the identification of a “source signature” for oxygenates that would permit reliable source identification, and perhaps even source

apportionment, when used in conjunction with fate models. Although the identification of a source signature would be very useful, the feasibility of doing so is unclear, and attempts to provide similar signatures for other environmental contaminants do not provide much cause for optimism. Consequently, this has to be rated as a lower priority than the development of the multimedia model described above.

3. TRANSPORT

3.1 Background

Oxygenates may enter both surface and ground water from diffuse and point sources (see Section 2, Source Characterization). In the case of scavenging from the atmosphere to precipitation, numerical modeling by Pankow et al. (1997) indicates that MTBE would transfer from the unsaturated zone into the saturated zone. However, no field observations of MTBE concentrations in ground water during and after precipitation or snow melt events are known to have been conducted.

The transport of oxygenates, particularly MTBE, through aquifers would be expected to occur at nearly the same velocity as the ground water. In a mixed-composition contaminant source, such as is found in oxygenated fuels, each individual component will travel at a rate dependent on its water solubility and sorption tendency for soil. Oxygenates generally are more soluble in water and less sorbed to soils than the other major organic compounds in gasoline, namely, benzene, toluene, ethylbenzene, and xylenes (BTEX). Given sufficient time and distance, each component of the mixture will separate within the plume according to basic chromatographic principles. Consequently, MTBE and other oxygenates would be expected to be at the leading edge of the plume or, in the extreme case over a long period of time, could become completely separated from the rest of the plume if the original source of oxygenate were eliminated. If biodegradation of the oxygenate occurs (see Section 4, Transformation), it will interact with the transport process such that the front may appear to recede or be stabilized.

Generally, aquifer vulnerability to oxygenate contamination can be predicted using current wellhead protection models on a case-by-case basis. The required parameters for these models are hydrologic, geologic, and contaminant-specific. The required chemical data for modeling

oxygenate transport are generally known, but transformation rates for the subsurface soil, vadose zone, and aquifers are required to run these models. The vulnerability of deep aquifers to oxygenate contamination is not well documented. In particular, the threat to deep aquifers due to abandoned wells and/or karst topography has not been assessed. Similarly, the threat to surface streams and lakes has not been assessed, even though suitable fate models for both exist. Again, adequate oxygenate loading models and fate parameters are needed to apply these models, particularly biodegradation rates, photolysis rates, and net air-water exchange rates.

3.2 Needs

Given the progress made in the last several years on modeling the fate (transport and transformation) of organic compounds, particularly BTEX compounds, in soils, ground water, and surface water, reasonable estimates of transport between and through environmental media can be made for oxygenates. For example, MTBE is expected to move through soil and ground water at a higher rate than BTEX compounds because it is more water soluble and less retarded by the solid matrix. However, the impact that biodegradation will have on MTBE plume movement is less well understood. The greatest need, therefore, is to determine biodegradation rates for MTBE, other oxygenates, and their by-products under typical soil-groundwater transport conditions (as outlined in Section 4, Transformation). Field studies are needed to validate modeled rates of MTBE infiltration during precipitation events to determine the extent that diffuse sources contribute to groundwater contamination, particularly shallow aquifers used for private wells. Three dimensional delineation of MTBE plume morphology in a variety of hydrological settings can be accomplished using push sampling techniques at multiple levels. Deep aquifer vulnerability should be examined by applying state-of-the-art fate models for scenarios that include karst-fractured flow effects and abandoned wells in areas that have high oxygenate use.

Field studies of the type the USGS Toxics Program (Baehr et al., 1997) is conducting are needed to quantify the combined impact of precipitation, land use, and storm water management practices on oxygenate loadings to surface and ground waters, and to develop and test multimedia exposure models. Stream and lake threat assessments also should be conducted to bound the potential threats from both diffuse and point sources of oxygenates and their degradation products.

4. TRANSFORMATION

4.1 Background

Contaminants may be transformed through a variety of chemical, physical, or biological processes. As a result, the mass, toxicity, mobility, volume, or concentration of parent contaminants in soil and water may be altered. The resulting products of these transformation processes may in turn pose either a greater or lesser risk. For surface water, potential transformation processes are biodegradation, photolysis, and hydrolysis. In ground water, the potential transformation processes include biodegradation and hydrolysis. In surface water, photolysis is the most important transformation process for ether oxygenates, and biodegradation is the most important process for alcohols. Basic photolytic and hydrolytic processes are adequately understood.

Studies on the rates and pathways of environmental MTBE biodegradation are inconclusive, in part because they have been conducted under different conditions. For example, Suflita and Mormile (1993) reported no biodegradation of MTBE in lab microcosms under a variety of aerobic and anaerobic conditions, using sediments from a petroleum-contaminated site. Salanitro et al. (1994), however, reported complete mineralization of MTBE to CO₂ in a mixed culture that was continuously sparged with oxygen. In another study (Petroleum Environmental Research Forum, 1993), MTBE was biodegraded when inoculated with a specific bacterial enrichment but not when inoculated with activated sludge. Limited biodegradation was observed in sediments under methanogenic conditions (Mormile et al., 1994) and in aerobic microcosms constructed with aquifer material obtained from the vicinity of the source area of a plume of dissolved BTEX and MTBE (Borden et al., 1997). Steffan et al. (1997) found that a number of propane-oxidizing bacteria were able to degrade high concentrations of MTBE, ETBE, and TAME. A series of degradation products were formed but did not prove to be effective growth substrates. Marked reduction in the concentrations of MTBE and benzene following termination of active remediation of fuel contamination was observed at a site in North Carolina (Cho et al., 1997). Products of MTBE biodegradation have been reported to include TBA (Mormile et al., 1994), but comprehensive identification of biodegradation products and reaction pathways has not been undertaken.

Results from field studies of the natural biodegradation of MTBE in ground water show that the processes involved generally take place at very slow rates or with long lag times, and depend on site-specific geochemical conditions. Schirmer and Barker (1998) found that during the first 16 months following a controlled injection of oxygenated gasoline in a sandy aquifer in Ontario, there was little evidence for the biodegradation of MTBE. However, when the aquifer was sampled seven years later, the mass of MTBE had declined by more than an order of magnitude. Although the authors hypothesized that natural biodegradation may have been responsible for this disappearance, they noted the need for confirmatory lines of evidence to support this hypothesis. In contrast, Landmeyer et al. (1998) studied an accidental spill in South Carolina over a five year period and concluded that dispersion and dilution were primarily responsible for decreases in the concentration of MTBE, with biodegradation playing a very minor role.

Ethanol may pose a different issue with respect to oxyfuel biodegradation. Recent reports have noted that the presence of ethanol in gasoline may inhibit the biodegradation of BTEX compounds in groundwater, perhaps because microbes preferentially metabolize the ethanol (Corseuil and Alvarez, 1996; Corseuil et al., 1996, 1998; Hunt et al., 1997). As a result, these BTEX plumes may persist longer and become larger.

The above discussion is not a comprehensive summary of studies on the biodegradation of MTBE and other oxygenates, but it does illustrate the variety of results observed. Most of the studies were conducted in laboratories, and the results are not necessarily representative of what might occur in the field. In addition, the observed rates of degradation vary widely, and this variability will impact the applicability of biodegradation as a remedial option (see Section 10, Contaminant Removal).

4.2 Needs

Biodegradation rates and pathways for MTBE and other oxygenates need to be measured experimentally to understand and predict the fate of these compounds in the environment, and to design cost-effective removal and remediation technologies. The rates of biodegradation will be key in understanding the fate of oxygenates in the subsurface, in developing in situ and ex situ contaminant treatments, in implementing natural attenuation protocols, and in conducting aquifer vulnerability modeling. Identification of by-products and characterization of their environmental fate are needed to develop a complete picture of the effects of oxygenates on the environment and

consequently the risks they may pose. Natural or intrinsic bioremediation is being widely accepted as either a primary or “polishing” process for groundwater remediation. Rapid transport, coupled with a slow rate of biodegradation, if confirmed, could limit the application of this remediation strategy as it relates to MTBE and possibly other oxygenates.

Additional field-scale and complementary laboratory microcosm studies are needed for sites with a variety of geochemical conditions and contamination scenarios. The geochemical conditions should reflect those commonly found in contaminated groundwater systems, including a range of redox and pH conditions, to determine the relative importance of aerobic and anaerobic processes in MTBE degradation. The contamination scenarios should include regions not only near the source where concentrations will be the highest but downgradient from the source where concentrations are likely to be much lower, as well as during vadose zone infiltration by contaminated storm water. The laboratory studies also should investigate the rates of biodegradation for high, moderate, and low concentrations of oxygenates, particularly as the concentration approaches a cleanup standard. Transformation products need to be identified and quantified so that specific biochemical pathways and degradation product yields under different conditions can be determined. Along this line, more attention should be given to other oxygenates that are not yet being used on as wide a scale as MTBE and ethanol but that could come into more widespread use. The possibility that ethanol or other oxygenates may inhibit the biodegradation of BTEX should be evaluated.

5. OCCURRENCE

5.1 Background

Although scattered incidents of localized water contamination by MTBE have been reported since the early 1980s, the first report to suggest that oxygenate contamination of water might be occurring on a widespread basis came as a result of the USGS National Water Quality Assessment (NAWQA) program. Designed to assess the status and trends in the quality of ground and surface water resources of the nation, the NAWQA program began sampling ground waters for MTBE in 1993 (and added TAME, ETBE, and DIPE in 1996). In an initial analysis of the NAWQA program’s first 20 study areas or units, MTBE was the second most frequently

detected volatile organic compound (VOC) in shallow ground water from selected urban areas monitored during 1993 and 1994 (Squillace et al., 1996). Of 210 sampled wells and springs, 56 (27%) contained MTBE at a minimum reporting level of 0.2 µg/L. (For comparison, 28% contained chloroform and 5% contained benzene.) Sixty wells and one spring contained MTBE and/or BTEX; of these 61 sites, 79% had MTBE alone, and 13% had both MTBE and BTEX. Of all the urban wells and springs sampled, 3% had MTBE concentrations exceeding 20 µg/L.

Since the USGS findings, other studies have provided data that supplement the picture of MTBE occurrence in ground, surface, and drinking water. However, it is difficult to characterize the overall occurrence of oxygenate contamination because reports vary in their focus, methods, geographic coverage, and time frames. Also, some monitoring programs are ongoing, with reports updated continually via the internet. Therefore, this discussion can offer only an impressionistic treatment of the subject. Although the relative contributions of point and non-point sources are yet to be determined (see Section 2, Source Characterization), sites of known or possible UST releases obviously warrant particular attention. For example, Happel et al. (1998) analyzed data from 236 leaking UST sites in California and found that MTBE was detected at 78% of these sites. Of the 32,409 known leaking UST sites in California, 13,278 are known to have contaminated groundwater. Based on their analysis, Happel et al. estimated that the minimum number of California UST sites with MTBE present was greater than 10,000.

Buscheck et al. (1998) evaluated groundwater plume monitoring data from more than 700 service station sites in four states in different regions of the country. MTBE was detected at approximately 83% of the sites, with about 43% of all sites having MTBE concentrations greater than 1,000 µg/L. The highest frequencies of detection occurred at sites of currently operating stations (n = 466) in Texas and Maryland (96 and 98%), with northern and southern California intermediate (83 and 84%), and Florida the lowest (76%). Similar but slightly lower rates of occurrence were found at sites with nonoperating stations (n = 243). Concentrations greater than 1,000 µg/L were found at 55% of the operating sites and 22% of the nonoperating sites. The authors suggested that differences in the incidence and levels of MTBE occurrence may have been due to factors such as hydrogeologic differences, differing histories of MTBE usage, and UST upgrade efforts in the states considered.

An EPA-supported survey of the 50 states and District of Columbia found that, of the 34 states that acquire MTBE data from leaking UST sites, 27 (79%) indicated that MTBE was

present at more than 20% of their sites and 10 (29%) reported MTBE at more than 80% of their sites (Hitzig et al., 1998). Interestingly, five states reported detecting MTBE (at $>20\text{ }\mu\text{g/L}$) with non-gasoline petroleum such as diesel fuel, jet fuel, and heating oil. The survey also asked about contamination of drinking water wells. Of the 49 state programs that responded to the survey, 25 (51%) had received reports of private wells contaminated with MTBE. It was estimated that the total number of contaminated private wells ranged from 2,256 to 2,663. In addition, 19 (39%) programs had reports of public drinking water wells contaminated with MTBE, with the estimated total number of such wells ranging from 251 to 422. These totals are presented as ranges because the survey requested data in ranges (e.g., 1-10, 11-20, etc.) or as highest estimates (e.g., estimate if greater than 40).

The contamination of drinking water wells also was examined by the USGS in an extension of the NAWQA study described above (Squillace et al., 1996). Data were collected in 1995 from additional wells in the same 20 NAWQA study units, combined with previously collected data from these units, and analyzed for the entire period of 1993-1995 (Zogorski et al., 1998). The data were sorted according to whether or not the sampled wells were used for drinking water. This analysis showed MTBE detections in 12 (14%) of 83 urban wells used for drinking water and in 19 (2%) of 949 rural wells used for drinking water, with a median concentration of approximately $0.50\text{ }\mu\text{g/L}$. Only one of the more than 1,000 samples exceeded the EPA Drinking Water Advisory of $20\text{-}40\text{ }\mu\text{g/L}$.

The USGS findings for drinking water wells are consistent in certain respects with results from a recent study in Maine in which 951 household drinking water wells and 793 Public Water Supplies (PWSs) were sampled for MTBE (Maine Department of Human Services, Bureau of Health, 1998). At a minimum reporting level of $0.1\text{ }\mu\text{g/L}$, preliminary results showed MTBE detections in 150 (15.8%) of the sampled household wells. The incidence of private well samples exceeding state's maximum contaminant level of $35\text{ }\mu\text{g/L}$ for MTBE was 1.1%, somewhat higher than the incidence of such concentrations in the USGS analysis. The Maine report projected that approximately 1,400-5,200 private wells across the state could be contaminated at levels exceeding $35\text{ }\mu\text{g/L}$. For the Maine PWSs, 125 (16%) of the samples had detectable levels of MTBE, with no samples above the $35\text{ }\mu\text{g/L}$ standard and 48 (6.1%) between $1\text{ }\mu\text{g/L}$ and $35\text{ }\mu\text{g/L}$.

In another recent study, the American Water Works Service Company (Siddiqui et al., 1998) collected data from drinking water wells in 16 states. Forty-four (2%) of 2,120 samples

from 17 (4%) of 450 wells tested positive for MTBE at a minimum reporting level of 0.2 µg/L, with the highest concentration reported at 8.0 µg/L. The detections occurred primarily in eastern states in areas with known UST releases.

Since February 1997, the California Department of Health Services has required public water suppliers to monitor their drinking water sources (i.e., ground water and surface water) for MTBE. To date, over 4,566 (39%) of 11,837 drinking water sources in California have been sampled for MTBE (California Department of Health Services, 1998). Of these, 26 (0.6%) sources (18 ground water and 8 surface water) had detectable levels of MTBE, including 9 sources with samples exceeding California's drinking water interim action level of 35 µg/L. These data are based on a detection limit of 5 µg/L. If all detections are considered, including possible false positives below 5 µg/L, 65 sources (1.4%) had detectable levels of MTBE. None of the surface water samples exceeded 35 µg/L.

Other USGS regional studies are ongoing for New England aquifers (Grady, 1997), aquifers and surface waters of Long Island, New York and in New Jersey (Stackelberg et al., 1997), and fractured bedrock aquifers in Pennsylvania (Lindsey et al., 1997). Also, the USGS and EPA entered into a cooperative agreement to conduct a pilot study (managed under the USGS National Synthesis Program) in 12 northeastern states to describe the occurrence and distribution of MTBE and other VOC's in drinking water sources through a stratified statistical sampling of recent public water supply system data (both ground water and surface water) and ambient ground water data (Grady, 1997).

To require monitoring of drinking water for MTBE or other oxygenates, EPA must first promulgate regulations requiring the collection of the data, with monitoring schedules based on the size of the public water system. As required by the Safe Drinking Water Act (SDWA), amended in 1996 (U.S. Code, 1996), EPA published a drinking water Contaminant Candidate List (CCL) on March 2, 1998 (Federal Register, 1998). The CCL is a list of currently unregulated contaminants targeted for consideration in priority-setting for the Agency's drinking water program, including regulatory determinations, drinking water research, occurrence monitoring, and guidance development such as health advisories. The 1998 CCL identified MTBE as a contaminant with specific data gaps in the areas of health effects and occurrence data. These data gaps must be filled in order for EPA to make a scientifically informed determination as to whether or not MTBE should be regulated with a health-based National Primary Drinking Water

Regulation. The CCL also serves as a source list of chemicals to evaluate for possible inclusion in the Unregulated Contaminant Monitoring Rule (UCMR), required by the SDWA to be finalized by August 1999. The proposed UCMR is expected to be published by early 1999 and to include MTBE. Contaminants included in the forthcoming rule will be subject to required monitoring by the states. Data collected during implementation of the final UCMR will be stored in the National Contaminant Occurrence Database (NCOD). The NCOD will provide the basis for identifying contaminants for future CCLs, supporting the Administrator's decisions to regulate contaminants in the future, and to assist in reviewing existing regulations and monitoring requirements every six years, as required by SDWA.

The Clean Water Act, Section 305(b) (U.S. Code, 1977) requires states and other participating jurisdictions to submit water quality assessment reports to EPA every two years. Based on these reports, EPA prepares the National Water Quality Inventory Report to Congress. However, a state may or may not provide data on specific unregulated contaminants such as MTBE in 305(b) reports, depending on the individual state's water quality priorities.

The detection and reporting of oxygenate contamination in water presupposes that adequate analytic methods are available for this purpose. The ether oxygenates can be analyzed with several standard EPA methods. The most reliable methods use purge-and-trap capillary column gas chromatography/mass spectrometry (GC/MS) such as EPA Drinking Water Method 524.2 (Eichelberger et al., 1992), EPA Waste Water Method 624 (U.S. Environmental Protection Agency, 1998b), or EPA Solid Waste (SW-846) Method 8260B (U.S. Environmental Protection Agency, 1998c). The USGS GC/MS method SH2020 also has been determined to be reliable for ether oxygenates (Connor et al., 1998). These GC/MS methods provide positive identification of specific constituents and, as such, they overcome the problem of false identification of coeluting constituents. Standard EPA methods that use a GC/photoionization detector (PID) (i.e., Drinking Water Method 502.2, Waste Water Method 602, SW-846 Method 8021) also can be useful, but because identification with these methods is based on the expected time that a chemical takes to pass through the capillary column, false positives are possible from coeluting constituents. Depending on the purpose of the analysis (e.g., UST site assessment, drinking water supply monitoring), the problem of false identification can be minimized by first determining if MTBE or another ether oxygenate is present with a GC/MS method, then performing analyses on additional samples with a GC/PID method (Happel et al., 1998). Gas chromatography/flame ionization

detector (FID) methods can be useful for detection of the alcohols as well as the ether oxygenates. However, as with PID, FID is subject to misidentification of coeluting compounds, and because FID is sensitive to all organic compounds, detection of specific compounds can be more difficult than with other equipment. Despite these problems, a two-dimensional GC/FID method for water samples with high hydrocarbon content has been developed using a modified ASTM method D4815 (Galperin, 1998). This method has been approved for use in California. Both EPA methods 8260B and the modified ASTM method 4815 are capable of detecting TBA concurrently with the ether oxygenates, although the detection limit for TBA is significantly higher than the detection limits for the ether oxygenates—approximately 30 to 40 µg/L for TBA and less than 1 µg/L for the ethers (Rhodes et al., 1998). However, a direct aqueous injection GC/MS method (Church et al., 1997) exists for detection of low levels of the ether oxygenates and TBA.

5.2 Needs

As stated in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) and affirmed by the NAS/NRC Review Committee (National Research Council, 1996), oxygenates should be added to existing VOC analyte schedules and included as routine target analytes for VOCs in drinking water, waste water, surface water, ground water, and remediation sites. Monitoring should be long term to support trend analyses of possible changes in water quality and the potential for population exposures. However, some discretion should be exercised with respect to including oxygenates that have not been used or are not expected to be used to any appreciable extent, if by their inclusion the cost of such monitoring would be significantly increased. Similarly, any decision to monitor for oxygenate transformation products on a widespread basis should be guided by information on the occurrence of the respective parent oxygenates and by definitive identification of the respective transformation products that would be targeted (see Section 4, Transformation). Given the existence of TBA as a primary oxygenate, as a contaminant of MTBE, and as a degradation product of MTBE, the inclusion of TBA in ambient ground water quality monitoring programs is advisable. It also would be useful to monitor for TBA at specific sites where MTBE contamination is known or suspected to have occurred.

The Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) recommended that a national database for monitoring data should be developed cooperatively among relevant governmental and private organizations, to be administered by a single federal agency. At present, existing “national” databases appear to be limited in their respective scopes. The EPA Safe Drinking Water Information System (SDWIS) contains drinking water data from public water supply distribution systems, whereas the USGS National Water Inventory System database contains ambient water quality data. As specified by the SDWA Amendments of 1996, EPA’s Office of Ground Water and Drinking Water is currently developing the first release version (by August 1999) of the NCOD, which will expand the existing capabilities of SDWIS. In the longer-term (i.e., 2000 - 2002) the Agency plans to upgrade the NCOD to include both public water system and ambient water quality data.

Assuming that oxygenates are added to VOC analyte monitoring lists, an effort should be made after a reasonable period (e.g., 3 to 5 years from now) to analyze these or other databases for trends in the occurrence of oxygenates in water. These analyses should be linked to exposure assessment efforts (see Section 6, Exposure) and evaluated for guidance as to whether more intensive monitoring or other actions are warranted. To the extent possible, monitoring efforts and database designs should be undertaken in a manner to relate qualitatively and quantitatively to exposure assessments for human populations and aquatic biota.

The most pressing research need related to analytical methods is to validate existing methods for the detection of alcohol oxygenates other than TBA, or develop new cost-effective methods for these alcohols. In addition, development of low cost, simple field methods for ether oxygenates would be useful. Although field portable GC/PID and GC/FID methods can likely be adapted for this purpose, supportive research would be helpful for facilitating their widespread use.

6. EXPOSURE

6.1 Background

Based on limited monitoring and occurrence data (see Section 5), a potential for exposure of biota and human populations to oxygenates exists. Exposure implies actual contact with a contaminant, not just the existence or occurrence of the substance in the environment. Exposure

characterization requires information on the magnitude and distribution of exposures. Among many factors that can affect exposure to oxygenate-contaminated water, unpleasant odor and taste have been reported as particularly notable in the case of MTBE in drinking water (e.g., Angle, 1991). However, it cannot be assumed that the sensory properties of oxygenates would prevent human population exposures to such contaminants. Individuals vary greatly in sensory and subjective reactions, and indeed, anecdotal evidence indicates that some individuals may have unknowingly consumed drinking water contaminated with MTBE at levels exceeding 35 µg/L (Maine Department of Human Services, Bureau of Health, 1998). Also, young children could be exposed via infant formula and beverages prepared with oxygenate-contaminated water. Even if all human exposures to oxygenates could be averted by water treatment processes, exposure of biota to contaminated surface or ground water could still occur.

Taste and odor detection thresholds for MTBE have been reported ranging from 24 to 135 µg/L for taste and from 15 to 180 µg/L for odor (Malcolm Pirnie, Incorporated, 1998b; Dale et al., 1997; Shen et al., 1997; Young et al., 1996; Prah et al., 1994; Vetrano, 1993a,b; TRC Environmental Corporation, 1993). Limited testing suggests taste and odor thresholds may be somewhat lower for ETBE and TAME than for MTBE (e.g., Shen et al., 1997; TRC Environmental Corporation, 1993; Vetrano, 1993a,b). None of the above studies attempted to characterize a population distribution of threshold responses.

It is important to note that detection and recognition thresholds for taste and odor sensations are distinct from their hedonic properties, which involve dimensions such as the (un)pleasantness and intensity of the sensory experience. The detection threshold is typically defined as the concentration at which a subject can detect a taste or odor difference between a standard (e.g., “plain” water) and the diluted test substance on a specified percentage (e.g., 50%) of the trials. The recognition threshold is the concentration at which a subject can recognize or identify the target substance in the diluent. In one study (Dale et al., 1997), four panelists were asked to describe the taste and odor of MTBE in odor-free water at concentrations ranging from 2 µg/L to 190 µg/L. At concentrations of 2 to 5 µg/L, the consensus judgment of the panelists was that the taste of MTBE could be described as “sweet.” At concentrations of 21 to 190 µg/L, the characterization was either “solvent” or “sweet solvent.” Similar characteristics were attributed to the odor of MTBE at concentrations of 21 to 190 µg/L. The panelists also were asked to rate the intensity of the taste and odor, which they considered “objectionable” at a

concentration of approximately 50 µg/L for taste and at approximately 90 to 100 µg/L for odor. Note that these tests were conducted with nonchlorinated, odor-free water at 25 °C.

Chlorination would likely raise the thresholds for the taste and odor of MTBE in water, and higher temperatures (e.g., for showering) would likely lower these thresholds. Also, thresholds will vary with instruction, training, motivation, age, gender, and other variables that are often not controlled for or reported.

Hedonic responses, along with considerations of consumer cost, convenience, and other factors, may figure importantly in the levels of contamination that individuals or communities will reject or accept (and consequently be exposed to) in their drinking water. Because cognitive factors, including attitudes that may be shaped by information provided through the social milieu, can significantly influence sensory perception (Dalton, 1996), populations as well as individuals may vary considerably in sensitivity to, and tolerance of, odors and tastes, such that a given concentration of contaminant might be quite acceptable to a large majority of persons in one group and strongly rejected by an equal proportion in another (cf. Anderson et al., 1995).

Microenvironmental measurements of VOCs such as benzene and trichloroethylene in relation to household water usage (e.g., Lindstrom et al., 1994; Wilkes et al., 1996; McKone and Knezovich, 1991) point to the importance of considering multi-media, multi-route personal exposures. "Drinking water" is used in many ways besides direct ingestion, including food preparation, dish washing, laundering, and bathing. In particular, showering affords a significant exposure potential by the inhalation and dermal routes, with variables such as water flow rate and temperature influencing exposure levels (Giardino and Andelman, 1996). Although physicochemical and other properties of oxygenates differ from VOCs investigated thus far, the importance of microenvironmental personal exposures to contaminated household water is relevant to oxygenates as well.

Aquatic, terrestrial, and marine biota are subject to exposure to acute and/or chronic releases of fuels and fuel additives. However, very little information exists to characterize exposure pathways or exposed ecological receptors in relation to oxygenates (Carlsen et al., 1997).

6.2 Needs

Limited empirical information is available either on the overall distribution of exposures to oxygenates in water for the U.S. population as a whole or on “high-end” exposure scenarios where oxygenate contamination is already known to occur. One step toward determining the prevalence and level of potential exposures to oxygenates would be to obtain monitoring data from public water suppliers (see Section 5, Occurrence). However, establishing large-scale monitoring programs is probably not the most efficient means for characterizing the potential for human population exposures to oxygenates. Rather, statistically representative sampling of public and private water supplies, including wells, may afford a more cost-effective approach. By coupling such data with qualitative and quantitative data on water usage and consumption patterns, it should be possible to model human exposures to specified oxygenates for risk assessment purposes (cf. Brown, 1997). The USGS NAWQA program may help address part of this need through a stratified statistical sampling of wells across the United States. Also, the National Health and Nutrition Examination Survey (NHANES) program may be used to collect data on population exposures to oxygenates and their metabolites, by sampling blood and drinking water for MTBE and TBA levels. Although the focus of this document is water contamination, exposure to oxygenates must ultimately be considered in terms of all relevant pathways and routes, including inhalation, ingestion, and dermal contact.

With respect to locales where oxygenate contamination of the public water supply has already been documented, the focus should be on evaluating potential personal exposure scenarios involving all household uses of oxygenate-contaminated water (e.g., for drinking, food preparation, cleaning, bathing). Several studies of multi-route VOC exposures through showering and other uses of tap water (e.g., Weisel and Jo, 1996) provide a substantial foundation for modeling as well as empirical studies of oxygenate exposure. As a first step, modeling of personal exposures, building on integrative approaches that incorporate macro- and micro-environmental pathways and even pharmacokinetic aspects (e.g., Georgopoulos et al., 1997; Piver et al., 1997; Rao and Ginsberg, 1997) should be undertaken, using sensitivity analyses to identify areas of needed additional data. Although a substantial database already exists for the pharmacokinetics of MTBE by inhalation (e.g., Borghoff et al., 1996), additional work is needed to supplement the limited pharmacokinetic data for the oral and dermal routes. Biomarkers of exposure

(e.g., metabolites such as TBA) might warrant investigation if exposures prove to be of sufficient concern.

More extensive data on odor and taste thresholds and hedonic responses to the various oxygenates are needed to determine whether or how population exposures may be affected by sensory variables. The question of what contaminant levels may be acceptable to different consumer populations is not an exposure assessment issue per se, but more data on thresholds and hedonic reactions would provide a stronger basis for determining consumer acceptance levels and for estimating actual usage of (and thus exposure to) oxygenate-contaminated water.

7. AQUATIC TOXICITY

7.1 Background

The aquatic toxicity of oxygenates has been briefly summarized in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Some basic toxicity data exist for MTBE, ETBE, TAME, DIPE, ethanol, and TBA for selected aquatic species (e.g., *Daphnia magna*, *Pimephales promelas*, *Carassius auratus*). However, EPA has not established water quality criteria for oxygenates for the protection of freshwater or marine aquatic life. Currently, testing is underway to evaluate the acute and chronic toxicity of MTBE to aquatic organisms (Christensen et al., 1998; Mancini et al., 1998). Based on the results of this work and other existing data (e.g., Huttenen et al., 1997), the EPA Office of Water expects to have a complete data set available for deriving water quality criteria for MTBE in early 1999.

7.2 Needs

Current actions should provide an appropriate basis for determining whether additional effects testing or research is needed.

8. HEALTH EFFECTS

8.1 Background

Most of the testing and research on the toxicity of oxygenates has been concerned with the effects of *inhaled* MTBE in laboratory animals and human volunteers. Little information exists on the effects of *ingested* oxygenates on humans, with the notable exception of the extensive database on the health effects of ingested ethanol. However, in the absence of any evidence indicating that human populations are exposed to ethanol-contaminated drinking water, the well characterized health effects of ingested ethanol need not be considered here.

A few studies have examined the toxicity of MTBE in laboratory animals via the oral route of exposure (Belpoggi et al., 1995; Robinson et al., 1990; IIT Research Institute, 1992; Bio-Research Laboratories Limited, 1990). None of these studies used drinking water as a medium for administering MTBE to animals; rather, they typically delivered MTBE mixed in olive oil or corn oil in a bolus dose through a tube into the stomach. This method does not correspond very well to the way that drinking water is typically consumed by people. Apart from such methodological problems, other questions have been raised about the use of some of these studies for risk assessment purposes (cf. National Research Council, 1996; Belpoggi et al., 1998). Considerable uncertainty hampers attempts to characterize the health risks related to MTBE in drinking water, as illustrated by the absence of a quantitative health risk estimation in a recent Drinking Water Advisory on MTBE (U.S. Environmental Protection Agency, 1997) and the somewhat divergent conclusions reached by different assessments of the data on MTBE toxicity (e.g., International Agency for Research on Cancer, 1998; Froines et al., 1998; California Environmental Protection Agency, 1998; European Centre for Ecotoxicology and Toxicology of Chemicals, 1997; Interagency Oxygenated Fuels Assessment Steering Committee, 1997).

Oral toxicity data for other ethers are even more limited, although some work on inhaled vapors of ETBE and TAME is currently being conducted under provisions of a Toxic Substances Control Act Enforceable Consent Agreement (Federal Register, 1995), and some work has been published on the kinetics and toxicity of inhaled ETBE (e.g., Hong et al., 1997; Johanson et al., 1997; Dorman et al., 1997) and TAME (e.g., Daughtrey and Bird, 1995). TBA is of relevance both as a metabolite of MTBE (Borghoff et al., 1996) and as an oxygenate or oxygenate by-product. Ingested TBA has been evaluated in rats and mice in a chronic bioassay by the

National Toxicology Program (Cirvello et al., 1995). Long-term exposure to TBA in drinking water produced various toxicologic and carcinogenic effects, including increased incidences of kidney and thyroid tumors.

8.2 Needs

Given the limitations of information on the oral toxicity of MTBE and the much greater database on the inhalation toxicity of MTBE, the question arises as to whether more oral toxicity studies should be initiated, or should inhalation toxicity data be extrapolated to estimate oral toxicity risk. A significant effort has already been devoted to investigating the kinetic behavior of MTBE in rodents with the goal of developing a physiologically based pharmacokinetic (PBPK) model to describe the dosimetry of MTBE and TBA in rats and humans (Borghoff et al., 1996). This ongoing work is expected to yield a more refined quantitative PBPK model in the near term. In addition, a pharmacokinetic study of human volunteers exposed to MTBE by the inhalation, oral, and dermal routes is being conducted by the EPA Office of Research and Development. As the results of these studies become available, it is anticipated that it will be possible to accurately predict levels of MTBE and TBA in rodent and human target organs for different routes and levels of exposure to MTBE. Consequently, it should be feasible to use inhalation toxicity data from past laboratory animal studies (Bird et al., 1997) to quantitatively estimate oral toxicity risks of MTBE in humans. Ultimately, the net health risks from multi-pathway exposures to MTBE (e.g., via refueling and motor vehicle use as well as drinking water) need to be assessed.

The options of initiating further oral toxicity studies or of using PBPK modeling to extrapolate from inhalation effects to oral toxicity risk are not mutually exclusive. A study of subchronic oral exposure to MTBE would provide better data on the potential for toxic effects as well as help validate a PBPK model for cross-route extrapolation. If such an extrapolation is unsuccessful, then a new chronic bioassay may be needed to reduce the uncertainties in assessing human health risks from chronic exposure to MTBE in drinking water.

Questions about the human relevance of carcinogenic effects observed in laboratory rodents exposed to high concentrations of MTBE also need to be resolved if uncertainties in current assessments of human cancer risk are to be reduced. In view of the weight necessarily attached to the cancer bioassays on MTBE, it would be desirable to reexamine and confirm the pathology data from all of these studies. Alternative assays for carcinogenicity, such as transgenic mice

(Tennant et al., 1995) and medaka fish (Boorman et al., 1997) assays, may offer relatively rapid approaches for collecting additional data that could contribute to a weight-of-evidence determination as well as insights on the modes of action. Although the latter approaches are unlikely to provide dose-response information that would enhance quantitative potency estimation (a critical need), and interpretation of negative results from these assays could be problematic, they could provide supporting or confirmative evidence of certain tumor types and thus assist in interpreting the relevance of inhalation effects for drinking water exposure.

The database for TBA may be adequate to characterize the oral toxicity of TBA. Given the potential for human exposure to TBA either as a metabolite, as an oxygenate itself, or as a natural biodegradation product of MTBE in ground water, an assessment of the carcinogenic and noncarcinogenic health risks of TBA should be undertaken.

The best strategy for the other ethers may be to obtain pharmacokinetic data (for some, work is already underway or anticipated for the inhalation route [U.S. Environmental Protection Agency, 1998d]) and take such information into account in designing and conducting oral toxicity testing of these ethers. This strategy is predicated on low usage of ethers other than MTBE. If occurrence or exposure data become available and suggest otherwise, the need for more intensive investigation of the pharmacokinetics and health effects of other ethers may be elevated. As for degradation products of oxygenates (other than TBA), more information on the occurrence and concentrations of these chemicals is needed to guide decision-making about which chemicals to test.

9. RELEASE PREVENTION

9.1 Background

Although the contribution of point source releases to the problem of environmental contamination from fuel oxygenates cannot be quantitatively characterized at present, such releases are clearly a matter of risk management concern. The compatibility of fuel storage and distribution system components with the fuel they contain has always been an issue for system component manufacturers, petroleum refiners and distributors, and regulators. Federal regulations (§280.32, Code of Federal Regulations, 1990) require that UST system components

be compatible with the constituents they contain. The changing composition of gasoline, particularly with the addition of ethers and alcohols, has raised the question of whether all existing systems are compatible with newer fuels and fuel additives.

Steel tanks and piping are not thought to be significantly corroded by oxygenates (Douthit and Davis, 1988; Geyer, 1995), but the effects of oxygenates on fiberglass reinforced plastic (FRP) tanks and piping have been less clear. Although MTBE and other fuel ethers have been shown not to cause corrosion of FRP (Douthit et al., 1988; Drake et al., 1995), manufacturers such as Owens-Corning (Bartlow, 1995) have indicated that they do not extend their 30-year warranties to older (pre-1984) FRP tanks exposed to alcohols, depending on the type and concentration of the alcohol used. No known published research has examined older tanks exposed to up to 10% ethanol.

The possibility exists that some UST system components, such as FRP tanks and piping and flexible piping, may be permeable to MTBE and other oxygenates. Such permeability might account for cases of MTBE contamination at gasoline stations where no leak could be detected and no other gasoline constituents were found. However, some doubt exists that the relatively large molecular weight of MTBE would allow it to pass through FRP (Curran, 1997). The only known study of FRP permeability to fuel oxygenates evaluated gasoline with 10 percent ethanol and found no liquid gasoline loss after 31 days (Smith Fiberglass Products Inc., 1996). No known work has been conducted on FRP permeability to any other oxygenate.

Elastomer seals, used for gaskets and o-rings throughout UST systems and petroleum pipelines, may have compatibility problems with oxygenated fuels. An American Petroleum Institute (1994) survey indicated that petroleum pipeline and terminal managers had noticed significant deterioration of many different types of elastomers associated with fuel oxygenates. The study, however, did not discuss the specific types of oxygenates that caused specific problems, nor did it discuss the concentrations of the oxygenates. Many of the problems listed were likely caused by “neat” (pure) solutions of the oxygenates, but the study raises the concern that more dilute solutions could cause problems as well.

Another study (Alexander et al., 1994) tested six elastomers in various concentrations of MTBE, ETBE, TAME, ethanol, and methanol. The authors found that although three of the seals were not able to withstand neat MTBE, all of the seals were acceptable for use in solutions of all five oxygenates when concentrations were less than 20% (immersed for 168 hours at 23 °C).

Hotaling (1995) tested 15 elastomers at 46 °C for 6 months and found significant deterioration of three types of elastomers when exposed to concentrations of only 5% MTBE in gasoline. As a result, Hotaling found that these seals may be "... unsuitable for even low percentages of MTBE." In actual use, however, EPA is not aware of any reports of UST system elastomers failing and causing a release because of exposure to gasoline containing oxygenates.

In addition to liquid-phase oxygenates, compatibility with vapor phase oxygenates also should be considered. Because the vapor pressure of MTBE is much higher than many other gasoline constituents, gasoline vapors should theoretically have much higher concentrations of MTBE than are found in the liquid phase (Davidson, 1998). These vapors would occur in the headspace of tanks and vapor recovery systems. In addition, liquid-phase MTBE-enriched condensate could form inside these vapor recovery systems. Hotaling (1995) tested elastomers exposed to MTBE vapors and found significant deterioration to some elastomers throughout the concentration ranges tested (5 to 100%).

Dispenser sumps, used to catch small amounts of fuel below gasoline dispensers, are typically made of high density polyethylene. Although these sumps should be checked periodically to remove any fuel, it is possible that some measurable quantities of gasoline and oxygenates could be released via the sumps. Another potential concern is tank liners. These are plastic tanks within tanks, typically used inside steel tanks that may have started to corrode, and are used to avoid replacing the original tank. Certain liner materials may not be compatible with oxygenated fuels (Meli, 1996).

Some information suggests that leak detection systems may not be mitigating UST releases as much as might be desired. In a survey of UST leak cases in California (Farahnak and Drewry, 1997), 263 (84%) of 313 cases were discovered in the course of tank closure activities; 15 (<5%) of the cases were identified through leak detection methods. For 132 cases with available monitoring data, the average lag between the date of last monitoring and discovery of a leak was 29 months. No information was provided regarding the presence of oxygenates in the survey. Although the survey did not resolve whether problems were due to the systems, misuse or a lack of use of them, or a combination of these factors, the report highlights the importance of leak detection issues, which in turn are clearly relevant to addressing oxygenated fuel releases.

9.2 Needs

The issue of materials compatibility with oxygenated fuels may prove to be quite manageable. However, a number of unanswered questions need to be resolved to ensure that releases do not and will not occur. It is important to characterize fully the effects of ethers and alcohols on elastomers, FRP, and other components of pipelines and tanks, particularly after several years of aging. The potential for leakage is unknown for older (pre-1984) FRP tanks that may be exposed to high (e.g., 10%) concentrations of ethanol. Also, the possible permeability of MTBE through FRP tanks and piping or flexible piping cannot be ruled out with existing data. Additional research is needed to resolve contradictory findings on the compatibility of elastomer seals with MTBE. Vapor recovery systems need to be examined more closely in terms of compatibility with concentrated MTBE vapor. Dispenser sumps need to be evaluated to determine if they are a potentially significant source of releases. Independent research is needed on the compatibility of currently marketed tank liners with ethanol.

Although newer technologies and regulations are intended to reduce the problem of leaking UST systems for conventional fuels, the different chemical properties of the various oxygenated fuels raise questions not only about the compatibility of existing systems but also about leak detection methodologies. Even though the differences in the physicochemical properties of oxygenated and non-oxygenated fuels may be small, modest research efforts may be required to reevaluate and confirm the performance and accuracy of in-tank and external leak detection and monitoring technologies.

Based upon the results of the above studies, new and improved approaches and technologies could be developed to repair or replace problem areas and to prevent future problems through the use of more advanced materials and design concepts.

10. CONTAMINANT REMOVAL

10.1 Background

Various methods are available for removing contaminants from soils, ground water, waste water, and drinking water. Many of these techniques are potentially applicable to contamination from oxygenates. However, very limited information exists on the technical feasibility and costs

of implementing them for oxygenate removal under field-scale operating conditions.

The following background discussion is not meant to differentiate these processes in their applications, but rather to address their general efficiency for soils or waters contaminated with MTBE or other oxygenates. The discussion also notes those technologies that may be appropriate for in situ subsurface remediation, those that may be more applicable to above ground treatment of contaminated ground water, and those that may be more suitable for drinking water treatment at the wellhead or in a drinking water treatment plant.

Water treatment to remove MTBE and other oxygenates will frequently be conducted as part of an overall treatment process to remove other contaminants such as benzene. Consequently, it is worthwhile to ask if an ongoing treatment process also will be effective for oxygenate removal. However, because oxygenates have different physical and chemical properties, a technology suitable for one oxygenate may not be suitable for another.

Subsurface treatment methods are often classified as those that transform, immobilize, or fix the contaminants in situ, and those that extract the contaminant from the subsurface for ex situ treatment on the surface. Both types are potentially applicable to MTBE and other oxygenates. In situ biological treatment is known to be effective for the BTEX component of fuels, but its effectiveness for oxygenates is subject to debate. The feasibility of an in situ bioremediation process depends on many factors, including the biodegradation rate, the redox conditions, and the presence of other contaminants. Information is very limited on the field application of in situ bioremediation to oxygenates either as part of an active treatment process or for natural attenuation.

Soil vapor extraction (SVE) is commonly used to remove gasoline contaminants from the unsaturated zone at spill sites. Based on its high vapor pressure and low affinity for organic carbon in soil, MTBE would be expected to be readily removed from soil by vapor extraction. A computer model, VENT2D, has been used to simulate this process for a gasoline-MTBE mixture (Conrad and Deever, 1995). In this simulation, MTBE showed the highest rate of mass loss of five gasoline components, as would be predicted based on their relative vapor pressures. Hence, MTBE and other ethers with high vapor pressures are not expected to be problematic for this technology. Grady and Johnson (1995) empirically demonstrated that SVE was successful in recovering MTBE, and as expected, the recovery of MTBE was greater than the recoveries for BTEX compounds.

Low-temperature thermal desorption (LTTD) is an ex situ soil treatment technology that uses temperatures below ignition levels to separate volatile contaminants from soil. Due to the high vapor pressure of MTBE, LTTD should be very effective in removing MTBE from soil. However, because MTBE separates from gasoline and dissolves quickly in water, both SVE and LTTD must be used soon after a release; otherwise most of the MTBE may have already moved from the soil into the ground water.

Air sparging involves the injection of air below the water table. The mechanisms for removal are stripping and potentially oxygen-enhanced biodegradation. Bass (1996) found that air sparging removed MTBE from ground water, with down-gradient wells showing 99% removal of MTBE. Levels continued to decline for 13 months after the air sparging unit was shut off, presumably due to aerobic degradation. Similar results also were reported by Cho et al. (1997).

Because MTBE does not adsorb well to soil and is highly soluble in water, “pump and treat” technology (i.e., pumping contaminated ground water and treating it above ground) may be effective in conjunction with certain above-ground biological or physical/chemical contaminant-removal processes. Conditions such as the presence of complex hydrogeology that create “dead” zones that are isolated from zones of high hydraulic conductivity will reduce the effectiveness of pump and treat for MTBE, despite its favorable chemical and physical characteristics.

Studies have indicated that MTBE can biodegrade in ex situ biological treatment systems under aerobic and anaerobic conditions (see Section 4, Transformation). Once the conditions for biodegradation of oxygenates are fully defined, field work can be completed to determine the practicality of ex situ biological treatment for oxygenates removal.

Granular activated carbon (GAC) adsorption is a frequently used treatment process for organic contaminants. However, because of its limited adsorption capacity for MTBE, GAC is generally not cost effective for removing MTBE (Speth and Miltner, 1990). Therefore, it is not expected that adsorption would be generally used for removing MTBE on a large scale. This is especially true at high influent concentrations that would limit the time that a GAC column could be effective. For public water supplies, field studies have shown that carbon adsorption is not cost effective for MTBE removal unless the concentrations are very low (McKinnon and Dyksen, 1984). For example, even with an influent concentration of 30 µg/L, the carbon beds need to be regenerated frequently. Other ether oxygenates have slightly lower solubilities than MTBE and

thus would be more effectively adsorbed. However, alcohol oxygenates such as ethanol and TBA are infinitely soluble, and thus adsorption would be ineffective for these compounds. Carbon adsorption may be useful as a polishing step to air stripping.

Malley et al. (1993) have shown that MTBE adsorbs more strongly to synthetic adsorbents than to GAC. Because the capital cost of the synthetic adsorbents was much higher than that of GAC, the authors concluded that synthetic adsorbent removal of MTBE was not economically feasible. However, synthetic adsorbents could be economically feasible for oxygenate removal if an inexpensive in situ regeneration process such as steam could be used (Malley et al., 1993).

For volatile organic compounds, air stripping is a cost effective alternative. However, the Henry's Law constant for MTBE is low (see Appendix 1), indicating a relatively low efficiency for air stripping. Air stripping at a very high air-to-water ratio (e.g., 200:1) has been found effective in removing 93 to 99% of MTBE from ground water (McKinnon and Dyksen, 1984; American Petroleum Institute, 1990), but at air-to-water ratios of 44:1, 75:1, and 125:1 the percentage of MTBE removed was 44, 51, and 61%, respectively (McKinnon and Dyksen, 1984). By comparison, an effective air-to-water ratio for benzene is typically near 50:1. High air-to-water ratios can lead to severe operating problems such as scaling and freezing during cold weather operations. McKinnon and Dyksen (1984) found that the cost of air stripping treatment was approximately 55% of that for carbon treatment. However, the off gas of the air stripping unit was not treated. Treating the off-gas stream would approximately double the cost of the air stripping system. Air stripping followed by GAC adsorption was found to be very effective for MTBE removal in this study, as also was found by Truong and Parmele (1992). Other oxygenates such as ETBE, TAME, and DIPE have higher Henry's Law constants than MTBE (approximately 3 to 20 times higher), indicating that air stripping would be at least slightly more effective for them. For example, in the study by McKinnon and Dyksen (1984) the percentage removal of DIPE at an air-to-water ratio of 200:1 was greater than 99% (McKinnon and Dyksen, 1984). However, alcohol oxygenates have very low Henry's Law constants, indicating that air stripping would not be effective for these compounds.

Yeh (1992) found that hydrogen peroxide in the presence of iron (Fenton's reaction) degraded ETBE and MTBE. This was later confirmed under laboratory conditions by Chen et al. (1998) and other researchers. Therefore, the hydroxyl radicals produced by Fenton's reaction appear to be an effective treatment agent. Ozone/ultraviolet (UV), ozone/peroxide, UV/peroxide,

and ozone/sonication also have potential as treatment technologies for oxygenate destruction. The American Petroleum Institute (1991) reported that advanced oxidation is more cost effective than other zero emission technologies such as steam stripping, ex situ biological oxidation, and air stripping with off-gas control. Malcolm Pirnie Incorporated (1997) also concluded that advanced oxidation is more cost-effective than carbon adsorption or air stripping with off-gas control. Malley et al. (1993) reported over 95% removal of MTBE using UV/peroxide. Oxidation byproducts included methanol, formaldehyde, and 1,1-dimethylethyl formate. Using UV/peroxide with a highly contaminated ground water produced less removal (up to 83%) presumably due to the effects of alkalinity scavenging of hydroxyl radicals and competition from other organics (Malley et al., 1993). The American Petroleum Institute (1997) reported up to 98% removal of MTBE in a UV/peroxide reactor under various conditions. Diisopropyl ether had higher removal rates than MTBE, indicating that DIPE is more easily destroyed by hydroxyl radicals than MTBE. Compared to benzene, MTBE is only moderately reactive, with reaction rate constants seven times lower than that for benzene. Kang and Hoffmann (1998) found that the combination of ozonation and sonication can effectively degrade MTBE into tert-butyl formate, TBA, methyl acetate, and acetone. Leitner et al. (1994) found that ozone/hydrogen peroxide treatment could eliminate ETBE and MTBE, with ETBE more reactive than MTBE. The ozonation byproducts were tertiary butyl formate, tertiary butyl acetate, and TBA.

Because advanced oxidation systems increase the biodegradability of the organic matter in the water, biofiltration may be recommended following oxidation to control for biogrowth in drinking-water distribution systems. The result could be an effective two-stage process: abiotic oxidation followed by aerobic biodegradation of the oxygenates.

10.2 Needs

Numerous areas of contaminant-removal research are needed for MTBE and other oxygenates. Because remediation and drinking water sites often differ with regard to contaminant concentration, clean-up goals, secondary-effect issues such as biological regrowth and corrosion, and public acceptability, this section is separated into remediation and drinking-water subsections. For both subsections, comparative cost estimates for all technologies are needed.

The research needs for the removal of oxygenates from waste water are not discussed separately here. Although waste waters typically contain higher levels of background organics

and inorganics that might interfere with the removal of oxygenates, it is not clear that oxygenate contamination of waste water is a widespread occurrence. To the extent that biological treatments (e.g., activated sludge, trickling filters) that are commonly practiced for wastewater streams may be effective in removing oxygenates by virtue of the biodegradation and stripping mechanisms within these technologies, many of the research needs discussed below will be pertinent to the removal of oxygenates from waste water. This is especially true of biological degradation, extensively covered in Section 4 (Transformation).

10.2.1 Remediation Needs

Remediation research is needed for both in situ remediation and ex situ cleanup of extracted ground water. This research should build on and expand earlier and ongoing work on remediation of ground water contaminated by other organic compounds. Research is likely to be most productive if it focuses initially on evaluating the applicability of known remediation technologies and adapting them to remediation of MTBE and other oxygenates. Cost as well as technical feasibility should be examined.

There is a pressing need for data on biodegradation (see Section 4, Transformation). Optimal conditions for biodegradation processes for in situ and ex situ contaminant removal need to be determined. This information is needed both to develop enhanced bioremediation technologies and to better understand the applicability of natural attenuation and risk based corrective action at UST sites with oxygenate contamination. A particular focus should be on the introduction of oxygen and nutrients for in situ plume treatment and the potential for abiotic oxidation and aerobic biodegradation in porous-reactor barriers. Data are needed from field research and supporting laboratory studies under a variety of conditions, including different geochemical conditions, presence of other contaminants, and oxygenate concentrations. Information gathered from research regarding optimal biological conditions for oxygenate removal may lead to cost-effective remediation processes. Research on in situ abiotic oxidation is a lower priority.

Extraction processes, including pump and treat, SVE, LTTD, in-well stripping, dual-phase extraction, and air sparging, need to be further evaluated. Specifically, the optimal operating conditions, effectiveness, and costs of these processes should be investigated for MTBE and other oxygenates. Also, off-gas control for SVE, air sparging, in-well extraction, and LTTD need to be

addressed when appropriate. Finally, the effect of temperature on Henry's Law constants for the entire class of oxygenates should be studied.

There is a particular need for research to develop and evaluate both biotic and abiotic surface treatment systems for extracted ground water. Air stripping is known to work, but many locations may require off-gas treatment. Research is needed to determine the effectiveness and cost of off-gas control. Promising research on bioreactors should be continued. For ex situ abiotic oxidation, Fenton's reagent, ozone/UV, ozone/peroxide, UV/peroxide, and ozone/sonication need to be further evaluated in terms of efficiency and cost under a variety of operating conditions. By-products of oxygenate degradation should be identified under different conditions. By-product destruction also may need to be evaluated. These oxidative processes should be optimized so that a site demonstration can be conducted to determine their cost effectiveness. GAC is not likely to be cost effective as an ex situ treatment process for MTBE in water but may have applicability to situations with low flow and low concentrations.

Sorbents such as vermiculite, straw, and peat have been proposed for oxygenate removal. Although their low cost may offset their low adsorption capacities, this is a low priority research area and should be limited to gathering and evaluating existing information at this time.

10.2.2 Drinking-Water Treatment Needs

Drinking-water treatment research needs to focus on low concentrations of contaminants typically found in source waters. Consideration should be given to the scale of water treatment; from large drinking water plants that treat hundreds of millions of liters a day to point-of-use systems that treat liters per day. Two technologies that should be investigated first include air stripping and hydroxyl-radical processes. For air-stripping, a matrix of the effectiveness and cost needs to be completed for various conditions (e.g., with and without off-gas control), which would allow more direct comparison to other treatment technologies. Also, configurations other than packed-tower aerators should be evaluated. Finally, the effect of temperature on Henry's Law constants for the entire class of oxygenates needs to be thoroughly studied so as to aid in the design and evaluation of heated air stripping and steam stripping systems.

For abiotic oxidation processes, a hydroxyl radical treatment, Fenton's reagent, has been shown to be effective for MTBE. Because of secondary effects, it is unlikely that Fenton's reagent would be used in a drinking water facility. However, other hydroxyl radical processes

that utilities have experience with, such as ozone/peroxide, ozone/UV, and peroxide/UV, need to be more extensively evaluated. Also, the applicability of the ozone/sonication process for drinking water treatment needs to be evaluated, including evaluation of UV lamp technologies. Oxidation byproducts, including bromate, should be identified and quantified under different conditions and byproduct destruction also may need to be evaluated. These oxidative processes need to be optimized so that a site demonstration can be conducted to determine their relative cost effectiveness.

Also, as previously mentioned, oxidation processes have been shown to increase the biodegradability of natural organics in water. Therefore, biofilters may be used in drinking water facilities to control distribution-system regrowth. The removal of oxygenates and oxygenate degradates or byproducts in these biofilters should be studied. Limited data exist for biodegradation under drinking-water conditions, but the increase in biodegradability of natural organics due to hydroxyl-radical treatment potentially holds promise for the removal of oxygenates and their degradates as a secondary substrate, even at low concentrations. Drinking water biodegradation work must concentrate on removing low levels of oxygenates.

Other biofiltration processes that utilize the addition of primary substrates should not be conducted under the auspices of drinking water treatment research. Primary substrates added to drinking water treatment streams are potentially problematic for several reasons: the primary substrate could contribute to deleterious human health effects; the primary substrate or its degradation byproducts might serve as disinfection byproduct precursor material; biogrowth might occur in the distribution system; and public dissatisfaction might result for these and other reasons.

Other drinking-water contaminant removal processes that need to be evaluated include GAC, carbonaceous adsorbents, and new bioreactor membrane technologies. For GAC, work needs to be completed in developing a matrix of the effectiveness and cost under various conditions. Because of its expected poor removal of oxygenates, GAC should be evaluated as a polishing step for air stripping technologies or as a biologically-active filter. Desorption from GAC also should be studied.

Synthetic carbonaceous adsorbents are very effective in removing many types of organic compounds from water. In general, steam is very effective for reversing adsorption processes for

weakly adsorbing contaminants such as MTBE. Therefore, a study of an automated system that would adsorb oxygenates then desorb (regenerate) under steam conditions should be initiated.

An automated reverse osmosis system may be applicable for small utilities (under 500,000 gal/day). However, the potential for success for reverse osmosis is limited due to the low molecular weights (32 to 102 Daltons) of most oxygenates, and thus only a quick, low-cost evaluation of this process is warranted. Other membrane devices such as carbon-fiber bioreactor membranes may be more effective; however, preliminary information is needed before extensive research is conducted.

11. CONCLUSIONS

The following priorities emerge from the foregoing discussion. No attempt is made to rank these needs relative to each other because they are all critical and are independent of each other in certain respects. For example, even though more information on biodegradation would assist in the development of contaminant removal methods, it does not follow that needed work on contaminant removal methods should be deferred to biodegradation studies. It is reasonable to expect that efforts can proceed concurrently in each of the areas identified here. It is also recognized that different organizations may rank priorities differently, depending on their mission, mandates, programmatic objectives, funding constraints, and other factors. For this reason, priority ranking of the following needs may vary among organizations, but all of them are valid and important. Therefore, each of the following needs should be given priority consideration.

- Determination of the relative contributions of point and non-point sources of oxygenate fluxes to surface and ground waters.
- Determination of oxygenate biodegradation rates and pathways under representative geochemical conditions, and identification of degradation by-products and their environmental fate.
- Inclusion of oxygenate analytes and principal suspected transformation products wherever VOC monitoring of water is routinely performed.
- Statistically representative sampling of public and private water supplies and modeling of multi-media, multi-pathway personal exposures for estimating population distributions of

exposures; modeling and empirical studies of “high-end” microenvironmental exposure scenarios.

- Completion of PBPK modeling and cancer mechanistic studies to enhance confidence in extrapolating from laboratory animal inhalation toxicity data as a basis for estimating oral toxicity risk of MTBE for humans; subchronic oral toxicity study of MTBE in drinking water.
- More extensive evaluation of oxygenate effects on materials used in tanks and pipelines, especially after aging over a period of years.
- Evaluation of the relative cost-effectiveness of candidate technologies for removing oxygenate contaminants from water under various conditions, with iterative efforts to optimize the most promising technologies, develop new innovative approaches, and evaluate the comparative cost effectiveness of available technologies.
- Updating of risk characterizations as results of the above work become available.

Efforts to address the issues identified in this document have been underway for some time, and new efforts are continually being initiated. Consequently, it is very difficult to describe the current state of the science in an accurate, up-to-date manner. Appendix 2 contains a listing of current projects related to oxygenates in water. The descriptions of projects are not adequate to convey the extent of work being undertaken; the intent is to provide an impression of the scope of studies underway and information to assist readers if they wish to obtain more details about any particular project.

The purpose of conducting the work identified in this document is to provide a better basis for characterizing the potential health and environmental risks of oxygenates and for informing risk management and policy decision making. Risk assessment and risk management efforts directed at oxygenates in water have been occurring and will likely continue. If the environment and public health are to be protected effectively and efficiently, however, adequate scientific information and technical data are essential.

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APPENDIX 1

CHEMICAL PROPERTIES OF SELECTED OXYGENATES

Chemical Name	Methyl Tertiary Butyl Ether	Ethyl Tertiary Butyl Ether	Tertiary Amyl Methyl Ether	Diisopropyl Ether
CAS Registry No.	1634-04-4	637-92-3	994-05-8	108-20-3
Synonyms	MTBE; 2-methyl, 2-methoxy propane; tert-butyl methyl ether; methyl tert butyl ether; methyl-tert-butyl ether	ETBE; tert-butyl ethyl ether; propane, 2-ethoxy-2methyl; 1, 1-dimethyl ethyl ether	TAME; 2-methoxy-2 methylbutane; methyl tert-pentyl ether; 1,1-dimethylpropyl methyl ether; methyl tert-amyl ether	DIPE; 2'2-oxybispropane; 2-isopropoxy-propane
Molecular Weight (g/mol)	88.15	102.18	102.18	102.18
Molecular Formula	C ₅ H ₁₂ O	C ₆ H ₁₄ O	C ₆ H ₁₄ O	C ₆ H ₁₄ O
Structural Formula	CH ₃ OC(CH ₃) ₃	(CH ₃) ₃ COCH ₂ CH ₃	CH ₃ CH ₂ C(CH ₃) ₂ OCH ₃	(CH ₃) ₂ CHOCH (CH ₃) ₂
Boiling Point (at 760 mm Hg)	55.2 °C	72.2 °C	86.3 °C	68.2 °C
Vapor Pressure (mm Hg at 20 °C)	240	130	75	159
Vapor Density (air = 1)	3.1	3.6	3.6	3.6
Density (g/ml at 20 °C)	0.74	0.74	0.77	0.73
Solubility (g/100 g water)	4.8	1.2	1.2	0.2
Henry's Law Constant				
(Atm-m ³)/ (g-mole)	5.28E-4 to 3E-3	2.64E-3	1.95E-3	4.77E-3
Dimensionless	2.2E-2 to 1.2E-1	0.11	0.081	0.199
Log K _{oc}	0.55 to 0.91	NA	NA	1.13
Log K _{ow}	0.94 to 1.30	NA	NA	1.52

CHEMICAL PROPERTIES OF SELECTED OXYGENATES (cont'd)

Chemical Name	Tertiary Amyl Ethyl Ether	Dimethyl Ether	Tertiary Butanol	Ethanol
CAS Registry No.	919-94-8	115-10-6	75-65-0	64-17-5
Synonyms	TAAE; ethyl tert-amyl ether; butane, 2-ethoxy-2-methyl	DME; methane, oxybis	TBA; tertiary butyl alcohol; 2-propanol, 2-methyl	ethanol; ethyl alcohol
Molecular Weight (g/mol)	116.20	46.07	74.12	46.07
Molecular Formula	C ₇ H ₁₆ O	C ₂ H ₆ O	C ₄ H ₁₀ O	C ₂ H ₆ O
Structural Formula	CH ₃ CH ₂ C(CH ₃) ₂ OCH ₂ CH ₃	CH ₃ OCH ₃	(CH ₃) ₃ COH	CH ₃ CH ₂ OH
Boiling Point (at 760 mm Hg)	102 °C	-24.8 °C	82.4 °C	78.5 °C
Vapor Pressure (mm Hg at 20 °C)	NA	758 to 5086*	41	44
Vapor Density (air = 1)	4.0	1.6	2.6	1.6
Density (g/mL at 20 °C)	0.75	0.66	0.79	0.79
Solubility (g/100 g water)	NA	4.7 to 35.3	miscible	miscible
Henry's Law Constant				
(Atm-m ³)/(g-mole)	NA	4.89E-4 to 9.97E-4	1.21E-5	6.91E-6
Dimensionless	NA	2.03E-2 to 4.15E-2	5.03E-4	2.83E-4
Log K _{oc}	NA	-0.29	1.57	-0.14
Log K _{ow}	NA	0.10	0.35	-0.32

*At 25°C

APPENDIX 2

CURRENT PROJECTS RELATED TO OXYGENATES IN WATER

This list of projects and activities is organized alphabetically according to the organizations conducting and/or sponsoring the work. Contact persons are identified parenthetically for obtaining further details, followed by a short title, brief description, and status of the project. After each item, topic identifiers are included for cross referencing to areas of needed work identified in the base document. This list was completed in December 1998 with the intention of being as complete and accurate as possible. However, given the breadth and dynamic nature of this area of work, some omissions and errors may have occurred.

Alpine Environmental (James Davidson)

MTBE Remediation; An Evaluation of Technologies, Field Experience, and Case Studies.

Review and analysis of remediation technologies applicable for MTBE; discusses both theory and actual case studies [American Petroleum Institute report, in press].

Contaminant Removal; Assessment

American Petroleum Institute (H. Hopkins)

MTBE Site Characterization Technical Bulletin.

Describes approaches for characterizing and monitoring subsurface MTBE sources and plumes, highlighting differences between MTBE and BTEX [expected completion second quarter 1999].

Source Characterization; Transport; Transformation

**Association of California Water Agencies; Western States Petroleum Association;
Oxygenated Fuels Association; California Environmental Protection Agency; U.S.
Environmental Protection Agency** (Krista Clark, ACWA; Dave Smith, ARCO)

MTBE Treatability Research Partnership.

Joint research program to evaluate existing and emerging treatment technologies to remove MTBE from public drinking water supplies [report expected by mid-1999].

Contaminant Removal

Chemical Industry Institute of Toxicology; Oxygenated Fuels Association (Susan Borghoff, CIIT; John Kneiss, OFA)

MTBE Cancer Mechanisms.

Study of role of alpha-2u-globulin in MTBE-induced kidney tumors in male rats [report expected late 1998].

Health Effects

Environmental and Occupational Health Sciences Institute; ARCO Chemical; State of New Jersey (Paul Liroy, Nancy Fiedler, EOHSI)

Inhalation Chamber Study of MTBE in Humans.

Inhalation exposure to MTBE in gasoline evaluated in controls and in subjects self-described as sensitive to MTBE; although only inhalation route used, results might be relevant to other routes [expected completion early 1999].

Health Effects

European Union; Finnish Environmental Institute; Finnish National Product Control Agency for Welfare and Health (Riitta Leinonen, FEI)

MTBE Risk Assessment.

Assessment of environmental and health risks of MTBE under Commission directive 93/67/EEC [publication expected 1999].

Assessment

International Agency for Research on Cancer (Julian Wilbourne)

MTBE Monograph.

Evaluation of carcinogenic risks of MTBE to humans [workgroup review October 1998; publication 1999].

Assessment

Lawrence Livermore National Laboratory; American Petroleum Institute (Anne Happel, LLNL; Bruce Bauman, API)

Study of MTBE and BTEX Plumes at California/UST Release Sites.

Characterize trends in the attenuation, magnitude of impact, and mobility of MTBE plumes in groundwater as compared to BTEX and evaluate the effectiveness of tank upgrades in preventing MTBE impacts [expected completion first quarter 2000].

Transport; Transformation; Release Prevention

Lovelace Respiratory Research Institute; Health Effects Institute (Janet Benson, LRRI; Maria Costantini, HEI)

Toxicokinetics of MTBE With and Without Gasoline.

Quantify uptake, metabolism, and excretion of C-14 labeled MTBE alone and in gasoline over a range of concentrations and repeated inhalation exposures in rats [ongoing through 1998].

Health Effects

Metcalf & Eddy; American Petroleum Institute (R. Claff, API)

Characterization of Service Station Stormwater Runoff.

Contractor to develop sampling plan to collect stormwater samples at several retail marketing facilities; samples to be analyzed for BTEX, MTBE, heavy metals, and a variety of other parameters [draft report expected late 1998].

Source Characterization; Occurrence

Metropolitan Water District of Southern California (Marshall Davis)

Surface Water Sampling.

Sampling for MTBE and other gasoline components in drinking water reservoirs used for recreational boating [ongoing through 1998].

Occurrence; Source Characterization

Metropolitan Water District of Southern California; U.S. Geological Survey; American Water Works Association Research Foundation (Bart Koch, MWDSC; Kenan Ozekin, AWWARF)

Sampling of Public Drinking Water Supplies.

Nation-wide sampling of source waters for community water systems to characterize MTBE contamination [expected completion 1999].

Occurrence; Exposure

MTBE Water Quality Criteria Workgroup (American Petroleum Institute) (Gene Mancini, ARCO; Alexis Steen, API)

Eco/aquatic Biota Toxicity.

After literature search to determine gaps in aquatic toxicity database, testing to develop data set to enable EPA to determine acute and chronic water quality criteria for MTBE in both fresh water and marine environments [report expected early 1999].

Aquatic Toxicity

National Research Council, Water Science and Technology Board (J. McDonald)

Intrinsic Remediation Study.

Assessment of current scientific understanding of natural processes that degrade or immobilize contaminants, including oxygenates, in soil and groundwater [report expected November 1999].

Assessment

National Toxicology Program (C.W. Jameson, NTP-NIEHS)

Proposed Listing of MTBE.

NTP to review recommendations of review committees and public comments regarding recommendations to the Secretary, DHHS, for listing MTBE in the Ninth Edition of the "Report on Carcinogens;" in December 1998 review, NTP Board of Scientific Counselors Subcommittee voted against motion to list MTBE as "reasonably anticipated to be a human carcinogen;" final public comment period open until February 15, 1999 [current status available at: <http://ntp-server.niehs.nih.gov/>].

Assessment

North Carolina State University; American Petroleum Institute (M. Hyman, NCSU; Bruce Bauman, API)

Cometabolism of Gasoline Oxygenates by Alkane-Utilizing Bacteria.

Evaluate and quantify the role of gasoline alkanes as stimulators, inhibitors, and regulators of in situ bacterial cometabolic biodegradation of MTBE in soil and groundwater [completion third quarter 2000].

Transformation

North Carolina State University; American Petroleum Institute (Robert Borden, NCSU; Bruce Bauman, API)

Monitoring Degradation: Sampson County, NC.

Monitoring degradation of MTBE, BTEX in plume from UST in shallow coastal aquifer in Sampson County, NC; leak discovered ~1986, remediated 1990 [see: Borden, et al., Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. Water Resour. Res. 33: 1105-1115, 1997; Borden et al., Field studies of BTEX and MTBE intrinsic bioremediation. Washington, DC: American Petroleum Institute; Health and Environmental Sciences Department. API publication no. 4654, 1997; final report expected late 1998].

Transport; Transformation

Oregon Graduate Institute; American Petroleum Institute (Rick Johnson, OGI; Bruce Bauman, API)

Removal of MTBE from a Residual Gasoline Source through in situ Air Sparging.

Evaluate the effectiveness of in situ air sparging to remove MTBE from source zone and the extent that such treatment results in reduction in MTBE in groundwater downgradient [expected completion early 1999].

Contaminant Removal; Transport; Transformation

Oregon Graduate Institute; Arizona State University; American Petroleum Institute (H. Hopkins, OGI; Bruce Bauman, API)

Field Tracer Experiment at Port Hueneme, CA.

Deuterated MTBE and tracer injected into existing MTBE plume followed by quarterly sampling for 1-2 years to determine changes attributable to biodegradation [report expected early 1999].

Transport; Transformation

Rutgers University; American Petroleum Institute (R. Cowan, RU; Bruce Bauman, API)

Ex Situ Biological Treatment of Water Containing MTBE.

Development of technology to biologically treat MTBE-contaminated water ex situ [ongoing through 2000; interim report expected late 1998].

Contaminant Removal

Rutgers University; Health Effects Institute (Jun-Yan Hong, RU; Maria Costantini, HEI)

Role of Human Cytochrome P450 2E1 in Metabolism and Health Effects of Gasoline Ethers.

Characterize metabolism of MTBE and other ethers in human liver microsomes, with attention to role of CYP 2E1 and its genotypic distribution in humans; compare ether metabolism in human liver microsomes versus rat and monkey nasal mucosa microsomes, to illuminate relevance of animal studies to humans [ongoing through 1998].

Health Effects

Shell Development Corporation (J.P. Salanitro)

MTBE Bioremediation.

Isolation of bacterial culture capable of degrading MTBE in groundwater [ongoing].

Contaminant Removal; Transport; Transformation

Shell Development Corporation (P.A. Westbrook)

Polymer-Solvent Interactions.

Prediction of polymer/elastomer response to MTBE-gasoline blends based on response to neat MTBE [see: Westbrook, P. A. and French, R. N., Elastomer swelling in mixed solvents, Rubber Chem. Technol. (in press); other reports in preparation].

Release Prevention

State of California, Department of Health Services (Steven Book)

Drinking Water Standards for MTBE.

Secondary and primary maximum contaminant levels (MCLs) for MTBE in drinking water to be established as required by 1997 state law; proposed secondary MCL of 5 µg/L to protect public from exposure to MTBE in drinking water at levels than can be smelled or tasted; proposed primary MCL, in preparation, to utilize Public Health Goal developed by California EPA's Office of Environmental Health Hazard Assessment (see separate listing) [secondary MCL adopted November 12, 1998 and currently under review by California Office of Administrative Law; proposed primary MCL to be released for public comment in spring 1999].

Assessment; Risk Management

State of California, Department of Health Services; U.S. Environmental Protection Agency-Region 9 (Leah Walker, CA DHS; Judy Bloom, EPA-Region 9)

California Drinking Water Source Assessment Program.

Compile data for MTBE in ground/surface source water from State Drinking Water programs; evaluate vulnerability to contamination and need for further assessment [ongoing; data available at <http://www.dhs.cahwnet.gov/org/ps/ddwem>].

Occurrence

State of California, Environmental Protection Agency, Office of Environmental Health Hazard Assessment (Juliet Rafol)

Public Health Goal for MTBE.

PHG for MTBE in drinking water intended to pose no significant risk to individuals, including most sensitive subpopulations, consuming the water daily over a lifetime; PHG considered by California Department of Health Services in setting primary MCL for drinking water; draft value, 14 µg/L [report to California Legislature due January 1999].

Assessment

State of California, Environmental Protection Agency, Office of Environmental Health Hazard Assessment (Susan Luong)

Proposition 65 Listing.

Science Advisory Board subcommittees evaluate whether MTBE meets criteria under California Proposition 65 for listing as "known to the state to cause cancer or reproductive toxicity" [subcommittees voted December 1998 not to list MTBE as either a carcinogen or reproductive toxicant].

Assessment

State of California Regional Water Quality Control Board; Lawrence Livermore National Laboratory; U.S. Environmental Protection Agency-Region 9 (Heidi Temko, CA RWQCB; Anne Happel, LLNL; Matt Small, EPA)

California GIS Mapping and Data Management Advisory Committee

Provide Governor's Office, legislature, and public entities with information on vulnerability of Calif. groundwater to MTBE; initiate state-wide geographical information system (GIS) to manage risk of MTBE contamination to groundwater supplies; investigate in two pilot project areas the feasibility and appropriateness of establishing a state-wide GIS mapping system [estimated completion June 1999; data available at <http://www-erd.llnl.gov/mtbe/>].

Source Characterization; Occurrence

State of California; University of California (Arturo Keller, UC-Santa Barbara)

Health and Environmental Assessment of MTBE.

As mandated by California State Legislature appropriating funds to the University of California, specific areas of study and reports as follow: (1) Evaluation of the Peer-reviewed Research Literature on the Human Health, including Asthma, and Environmental Effects of MTBE, John Froines, UCLA; (2) Integrated Assessment of Sources, Fate & Transport, Ecological Risk and Control Options for MTBE in Surface and Ground Waters, with Particular Emphasis on Drinking Water Supplies, John Reuter and Daniel Chang, UC-D; (3) Evaluation of Costs and Effectiveness of Treatment Technologies Applicable to Remove MTBE and Other Gasoline Oxygenates from Contaminated Water, Arturo Keller, UCSB; (4) Drinking Water Treatment for the Removal of Methyl Tertiary Butyl Ether from Ground Waters and Surface Water Reservoirs, Irwin Suffet, UCLA; (5) Evaluation of MTBE Combustion Byproducts in California Reformulated Gasoline, Catherine Koshland, UCSB; and (6) Risk-based Decision Making Analysis of the Cost and Benefits of MTBE and Other Gasoline Oxygenates, Arturo Keller, UCSB [initial report released November, 1998; final report expected spring 1999; report available at: <http://tsrtp.ucdavis.edu/mtberpt/>].

Assessment

State of Maine; Departments of Human Services, Environmental Protection, Conservation (Andrew Smith, Bureau of Health, Maine DHS)

Monitoring Public and Private Water Supplies: Maine.

Preliminary results of random statewide monitoring for MTBE and other gasoline constituents in public and private drinking water supplies statewide [preliminary report available at <http://www.state.me.us/dep/blwq/gw.htm>; final report expected early 1999].

Occurrence

University of California-Davis (John E. Reuter)

Sources, Fate, and Transport of MTBE in Sierra Nevada Multiple Use Lakes.

Study of sources, transport, and fate of MTBE in Lake Tahoe and Donner Lake [ongoing; see Reuter et al., Concentrations, sources, and fate of the gasoline oxygenate methyl tert-butyl ether (MTBE) in a multiple-use lake, Environ. Sci. Technol. 32: 3666-3672, 1998].

Transport; Transformation; Source Characterization

University of California-Davis; American Petroleum Institute (E. Schroeder, UC; Bruce Bauman, API)

Vapor Phase Biodegradation of MTBE.

Evaluate effectiveness of biofilters in MTBE vapor phase treatment; culture aerobic, natural microbial consortium that rapidly degrades MTBE, uses MTBE as its sole carbon and energy source, and has been shown (Eweis et al., Proceedings 90th AWMA Meeting, Toronto, June 8-13, 1997) to degrade MTBE in both liquid and gas streams (biofilters); assess impact of other organics (e.g., aromatics, alkanes) on MTBE biodegradation; characterize potential limitations of technology [report expected second quarter 1999].

Contaminant Removal

University of California-Davis; EPA-OSWER-OUST (Thomas Young, UC; David Wiley, EPA-OSWER-OUST)

Field Verification of UST System Leak Detection Performance.

Evaluate data from UST closures and release investigations from approximately 16 state environmental agencies to (1) quantify probability of types of leak detection failures (missed detections, false alarms) for different methods and equipment brands, and (2) understand sources of failure (e.g., human error, mechanical failure, environmental variables) [report and database expected late 1999].

Release Prevention

University of Houston; American Petroleum Institute (William G. Rixey, UH; Bruce Bauman, API)

Characteristics of MTBE from a Gasoline Source.

Characterize dissolution and desorption of MTBE from a gasoline source residually trapped in soil; assess duration of MTBE in source area; leaching behavior evaluated in laboratory fixed-bed columns and results modeled [expected completion late 1998].

Transport; Transformation

University of Massachusetts-Amherst; American Petroleum Institute (Derek Lovley, UM; Bruce Bauman, API)

Anaerobic Degradation of MTBE, BTEX, and PAHs in Petroleum-Contaminated Aquifers.

Determine: 1) potential for ferric iron to serve as electron acceptor for anaerobic biodegradation of MTBE and BTEX in groundwater and rates associated with this process in variety of aquifers; 2) anaerobic processes in the source area of fuel spills; 3) anaerobic biodegradability of PAHs in groundwater [report expected late 1999].

Transport; Transformation; Contaminant Removal

University of Medicine and Dentistry of New Jersey (Clifford P. Weisel)

Modulation of Benzene Metabolism by Exposure to Environmental Mixtures

Evaluate (1) metabolism of benzene when inhaled by humans alone or as part of a mixture of MTBE or metals such as iron, and (2) in vitro toxicity of metabolites of mixtures such as benzene and MTBE [ongoing].

Health Effects

University of Michigan-National Center for Integrated Bioremediation (Michael Barcelona)

MTBE Behavior in BTEX Plume.

Characterize natural fate and transport of dissolved MTBE/BTEX under different shallow groundwater redox regimes, and effects of oxygen-releasing material; information on the evolution of microbial ecology also to be collected [expected completion fourth quarter 1999].

Transport; Transformation

University of Nebraska (H. Nouredini)

Remediation Efficiency for ETBE compared to MTBE.

Comparative experimental studies of removal of ETBE and MTBE from contaminated water by air stripping and carbon adsorption; literature review of available ETBE research data [ongoing; unpublished report available upon request].

Contaminant Removal

University of Nevada-Reno (Glenn Miller)

Sampling for MTBE in Lake Tahoe.

Sample for MTBE from various depths and locations, including temperature and meteorology data; evaluate MTBE and BTEX contamination from watercraft [ongoing].

Occurrence; Source Characterization; Transport; Transformation

University of Northern Iowa; Exxon (C. M. Horan, UNI)

Effect of MTBE on Microbial Consortia.

MTBE added to microbial consortia increased oxygen consumption, but concentrations up to 740 mg/L inhibited mineralization potential of hexadecane up to 50%; although MTBE can be metabolized in environment, toxicity may adversely affect overall biodegradation of fuel HCs [ongoing; report available at <http://www.engg.ksu.edu/HSRC/95Proceed/horan.html>].

Contaminant Removal; Transport; Transformation

University of Notre Dame; Amoco Corporation (Charles Kulpa, UND)

MTBE Biodegradation by Pure Cultures.

Isolation of pure and mixed bacterial strains capable of degrading MTBE in soil and water [ongoing; see Mo et al., Biodegradation of methyl t-butyl ether by pure bacterial cultures, Appl. Microbiol. Biotechnol. 47: 69-72, 1996].

Contaminant Removal; Transport; Transformation

University of Oklahoma; American Petroleum Institute (Bruce Bauman, API)

Anaerobic Biodegradation of Gasoline Hydrocarbons and Oxygenates.

Summarize results of previous research on anaerobic processes and continue to evaluate anaerobic biodegradation of dissolved hydrocarbons, whole gasoline, and oxygenates [drafts of papers expected March 1999].

Contaminant Removal

University of Texas-Austin; American Petroleum Institute (Robert Mace, UT; Bruce Bauman, API)

Spatial and Temporal Variability of MTBE Plumes in Texas

Characterize spatial and temporal variation of MTBE plumes and their relation to other dissolved hydrocarbons, the nature of the release source, and site hydrogeology using existing database of 361 Texas UST sites [expected completion fourth quarter 1998].

Transport; Transformation

University of Washington (Crispin H. Pierce)

Toxicokinetics of Ethyl Tertiary-butyl Ether

Develop quantitative, predictive models that account for person- and gender-specific factors that influence ETBE toxicokinetics, using controlled exposures to stable isotope-labeled and unlabeled compounds and accurate measurements of these compounds and metabolites in blood, breath, and urine [ongoing].

Health Effects

University of Washington; American Petroleum Institute (Lee Newman, UW; Bruce Bauman, API)

Phytoremediation of MTBE.

Evaluate capabilities of selected plants to take up, degrade, or transpire MTBE [expected completion late 1999].

Contaminant Removal

University of Waterloo; American Petroleum Institute (Doug Mackay, UW; Bruce Bauman, API)

MTBE Natural Attenuation Field Research, Phase 1.

Identify suitable research site and generate initial site characterization data to determine:

1) mass flux of MTBE from a release site and its influence on the size of the resultant dissolved phase plume; and 2) natural attenuation processes that act to limit the migration of dissolved MTBE at that site [ongoing through 2000; interim reports expected annually].

Transport; Transformation

University of Waterloo; American Petroleum Institute (Jim Barker, UW; Bruce Bauman, API)

Monitoring Border Aquifer Plume.

Monitoring of MTBE, BTEX, MeOH, NaCl in experimental plume at Canada Forces Base Borden, Ontario; began ca. 1988, tracked for 16 months, resumed in 1996 [expected completion fourth quarter 1998; e.g., see Schirmer and Barker, A study of long-term MTBE attenuation in the Borden Aquifer, Ontario, Canada, Ground Water Monit. Rem. 18: 113-122, 1998].

Transport; Transformation

University of Wurzburg; Health Effects Institute (Wolfgang Dekant, WW; Maria Costantini, HEI)

Comparative Biotransformation of MTBE, ETBE, TAME, and DIPE in Rats and Humans.

Compare relative excretion of ether metabolites in humans and rats exposed in vitro and in vivo via inhalation, with attention to individual differences [ongoing through 1998].

Health Effects

U.S. Centers for Disease Control and Prevention (David L. Ashley)

Blood Levels of MTBE and TBA.

As part of NHANES IV, determine a reference range of blood levels of MTBE and TBA in non-occupationally exposed U.S. residents and examine relationship of these levels to local MTBE usage in gasoline and presence of MTBE in household water samples [pilot work begins January 1999; survey begins April 1999].

Exposure

U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances (Catherine Roman, EPA-OPPTS-CCD)

Proposed Children's Health Test Rule.

Toxicity testing of selected chemicals, including MTBE and TBA, with exposure potential for children [draft proposed rule in preparation; notice of proposed rule making expected March 1999 and final rule December 1999].

Health effects

U.S. Environmental Protection Agency, Office of Research and Development (Thomas F. Speth, EPA-ORD-NRMRL)

Cost Comparison of MTBE Removal Technologies.

Evaluation of ozone/peroxide oxidation and air stripping technologies for MTBE removal; air stripping to include off-gas control by adsorption and pilot-scale experiments [expected completion 2000].

Contaminant Removal

U.S. Environmental Protection Agency, Office of Research and Development (Fran Kremer, EPA-ORD-NRMRL)

Natural Attenuation of MTBE in Ground Water and Soils.

Field and laboratory studies on UST sites impacted with MTBE; preparation of technical resource documents on natural biodegradation of MTBE and associated HCs in ground water and soils, and on the potential for enhanced biodegradation [ongoing].

Transport; Transformation; Contaminant Removal

U.S. Environmental Protection Agency, Office of Research and Development (John Wilson, EPA-ORD-NRMRL)

Natural Attenuation of MTBE.

Field and laboratory study evaluating the role of natural attenuation of MTBE in a fuel plume at Elizabeth City, NC, and other sites [ongoing; report due FY2000].

Transport; Transformation

U.S. Environmental Protection Agency, Office of Research and Development (James Prah, EPA-ORD-NHEERL)

Human Pharmacokinetics of MTBE.

Pharmacokinetics study of human volunteers given multiple acute exposures to MTBE by inhalation, oral, and dermal routes [scheduled completion 1999].

Health Effects

U.S. Environmental Protection Agency, Office of Research and Development (Jim Weaver, EPA-ORD-NERL)

Simulation of Multicomponent Gasoline Dissolution.

Aquifer transport, leaching, and chemical property estimation models used to study multicomponent dissolution from MTBE- and non MTBE-gasolines, effects of MTBE on dissolution of BTEX, and minimum number of components required to simulate dissolution of a given gasoline component [report expected May 1999].

Transport; Transformation

U.S. Environmental Protection Agency, Office of Research and Development (Peter Gabele, EPA-ORD-NERL)

Marine Engine Emissions Characterization.

Characterize emissions in air and water from small outboard (<15hp) engines using 12%-vol MTBE-gasoline [expected completion fall 1999].

Source Characterization

U.S. Environmental Protection Agency, Office of Research and Development; IT Corporation (Anthony Tafuri, EPA-ORD-NRML)

Technologies for Remediating Petroleum-contaminated Soil.

Studies (bench and pilot field) of hydrogen peroxide with Fenton's reagent to oxidize MTBE in soil and water; identify intermediate products that may develop in treatment process and determine operational parameters (Chen et al., Chemical oxidation treatment of petroleum contaminated soil using Fenton's reagent, J. Environ. Sci. and Health, A33: 987-1008, 1998) [ongoing].

Contaminant Removal

U.S. Environmental Protection Agency, Office of Research and Development; New York State Department of Environmental Conservation (Jim Weaver, EPA-ORD-NERL; Joseph Haas, NY DEC)

Modeling Plume: East Patchogue and Uniondale.

3-D monitoring and modeling of MTBE, BTEX in contaminant plume from UST site on Long Island, NY, a demonstration site for EPA Hydrocarbon Spill Screening Model (HSSM) [J. Weaver, Transport and transformation of BTEX and MTBE in a sand aquifer, Ground Water Monit. Remed. (accepted); additional report in preparation].

Transport; Transformation

U.S. Environmental Protection Agency, Office of Research and Development; U.S. Environmental Protection Agency-Region 9 (Lance Wallace, EPA-ORD-NERL; Henry Lee, EPA-Region 9)

MTBE Exposure During Showering.

Personal exposure measurements of MTBE in shower microenvironment [expected to begin 1999].

Exposure

U.S. Geological Survey; American Petroleum Institute (Art Baehr, USGS; H. Hopkins, API)
Modeling Groundwater Impacts from MTBE Vadose Zone Transport.

Determine minimum mass source in vadose zone to create a persistent oxygenate impact to groundwater [begin December 1998; expected completion second quarter 1999].

Occurrence; Source Characterization

U.S. Geological Survey-NAWQA (John Zogorski, Wayne Lapham, USGS)

National Retrospective Analyses: Selected Areas.

Retrospective analysis of VOC and limited MTBE data in about 20 U.S. areas: CA, ID, IA, NJ, NY, TX, WI; several other areas available for further analyses; additional data being sought for 1998-1999 [ongoing through 2000; findings published yearly (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence; Source Characterization

U.S. Geological Survey-NAWQA (Mary Ann Thomas, USGS)

Groundwater Monitoring: Michigan.

Characterization of groundwater in residential suburban Detroit area 1996-1998; preliminary data analysis did not indicate presence of MTBE or TBA [data release expected mid-1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence; Source Characterization

U.S. Geological Survey-NAWQA (Arthur Baehr, Mark Ayers, USGS)

Glassboro Comprehensive Urban Study.

Monitor MTBE, VOCs in air, precipitation, surface water, unsaturated zone, ground water in Glassboro, NJ area aquifer [ongoing 1996-2000; project description published; shallow groundwater VOC data published; research published periodically (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation; Source Characterization

U.S. Geological Survey-NAWQA (John Zogorski, USGS)

Monitoring Urban Storm Water: Selected Areas.

Monitor urban storm water for VOCs, including MTBE, in 16 U.S. metropolitan areas: Boise, Phoenix, Colorado Springs, Denver, San Antonio, Dallas, Omaha, Independence, Little Rock, Davenport, Baton Rouge, Mobile, Huntsville, Birmingham, Montgomery, Atlanta [reports available upon request (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence; Source Characterization

U.S. Geological Survey-NAWQA; U.S. Environmental Protection Agency-Office of Water
(Steve Grady, USGS; Mike Osinski, EPA-OW)

Retrospective Analyses: New England-Mid Atlantic.

Retrospective data analysis for MTBE and other VOCs in ground/drinking water in 12 southern New England and Mid-Atlantic states; focus primarily on ambient ground water and PWS drinking water data for MTBE and other VOCs, with one objective to create protocol for state drinking water quality data collection [design completed; retrospective approximately 50% complete; report expected late 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence; Source Characterization

U.S. Geological Survey-NAWQA; Oregon Graduate Institute (John Zogorski, USGS; Jim Pankow, Wes Jarrell, OGI)

Plant Transpiration.

Measurement of plant transpiration on VOC levels including MTBE [report and journal article expected 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation

U.S. Geological Survey-NAWQA; Oregon Graduate Institute; University of Washington
(John Zogorski, USGS; Jim Pankow, OGI; Bill Asher)

VOC Behavior and Fate.

Modeling the behavior and fate of VOCs including MTBE in PWS reservoirs [journal article and report expected 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation

U.S. Geological Survey-NAWQA (Paul Squillace, Mike Moran, John Zogorski, USGS)

Occurrence of MTBE and Other VOCs in Ambient Groundwater.

VOCs in groundwater of the United States, 1985-1995 [journal article in preparation (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence

U.S. Geological Survey-NAWQA; Oregon Graduate Institute (John Zogorski, USGS; Jim Pankow, Rick Johnson, OGI)

Modeling MTBE Transport to a Production Well.

Preliminary evaluation of factors that influence the capture of MTBE UST release by a hypothetical production well [article expected early 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation

U.S. Geological Survey-NAWQA; Oregon Graduate Institute (John Zogorski, USGS; Jim Pankow, OGI)

VOC Analytic Methods: Air.

Analytic methods developed for VOCs, including MTBE, TAME, DIPE, and ETBE, in ambient air [article to appear in Analytical Chemistry, late 1998 or early 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence (Analytic Methods)

U.S. Geological Survey; Oregon Graduate Institute (John Zogorski, USGS; James Pankow, OGI)

Degradation Assessment.

Determine degradation pathways, by-products, kinetics, and their relationship to varied geological environments for MTBE, TBA, TBF, TAME, TAA, and acetone based on monitoring data from several plumes and lab studies [field monitoring and lab studies continuing in 1998; project findings and lab analytical method published (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation

U.S. Geological Survey; Oregon Graduate Institute (John Zogorski, USGS; James Pankow, OGI)

Modeling Non-point Source Inputs.

Modeling of atmospheric and land-based non-point source inputs of MTBE to ground water systems (see also USGS: Glassboro comprehensive urban study) [ongoing 1996-2000; research published periodically (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Source Characterization; Occurrence; Transport; Transformation

U.S. Geological Survey-Toxics Hydrology Program (Herb Buxton, John Zogorski, J. Landmeyer)

Monitoring Plume: Beaufort, SC.

Ongoing monitoring of shallow ground water and unsaturated zone above the ground water plume for VOCs, including MTBE, BTEX, TBA, for movement and degradation since 1991 at Laurel Bay UST (Beaufort Marine Corps Air Station, SC); remediated 1993; flow and contaminant modeling; long-term hydrology study site [ongoing; project scope and findings through 1997 published (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Transport; Transformation

U.S. Geological Survey (Carol Boughton)

Survey of Man-Made Organic Compounds in Lake Tahoe and Selected Tributaries, California-Nevada 1998-99.

Sample multiple sites on Lake Tahoe and major tributaries for the presence of organochlorine, semi-volatile industrial, synthetic-hydrocarbon compounds (including MTBE) and soluble pesticides [results expected to be published in 1999 (see <http://wwwsd.cr.usgs.gov/nawqa/pubs/>)].

Occurrence

Western States Petroleum Association (Jeff Sickenger)

Well Purging Study: California.

Comparison of MTBE, BTEX, and TPH-g in groundwater samples before and after purging at CA wells: concentrations higher before than after purging, variability of before/after concentrations comparable to variability between purging methods; high variability in small population of sites due to site-specific conditions [completed (Final Report: the California groundwater purging study for petroleum hydrocarbons, SECOR International, Inc., 1996; Lundegard et al., Net benefit of well purging reevaluated, Environ. Geosci. 4: 111-118, 1997;

see <http://www.secor.com/purge/purge.htm>); however, also see: Flood, F., *New study advocates no purging prior to sampling*, <http://www.grac.org/spring97/article2.htm>].

Contaminant Removal; Transport; Transformation

Woodward-Clyde; American Petroleum Institute (R. Claff, API)

Occurrence, Treatment, and Impact of Oxygenates in Effluents.

Characterize and quantify presence of oxygenates in petroleum marketing terminal and refinery wastewater streams and treatment processes; identify and quantify fate of oxygenates in terminal and refinery wastewater treatment facilities [expected completion late 1999].

Occurrence; Transport; Transformation

World Health Organization - IPCS (Edward Smith, WHO Geneva)

Environmental Health Criteria for MTBE.

Critical review of effects of MTBE on human health and the environment [in press].

Assessment

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